Santa Clara Valley Water District

Field, Pilot, and Laboratory Studies for the Assessment of Water Quality Impacts of Artificial Turf

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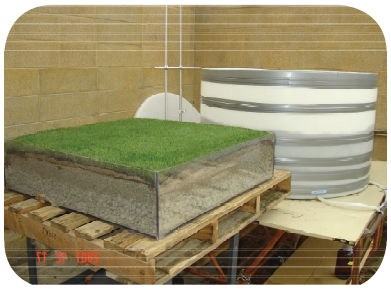

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EXECUTIVE SUMMARY

ES-1 Artificial Turf Fields as Substitutes for Natural Lawn

Constructing sports fields employing artificial turf technology instead of growing lawns is increasingly popular. Artificial turf consists of fiber blades (synthetic grass) that are attached to a plastic sheet (carpet backing) and padding with infill materials that contain crumb rubber. To remove rainwater, artificial turf fields are underlain by permeable rocks and equipped with a drainage system that connects to holding tanks and storm sewers. Geotextiles and layers of compacted clay prevent rainwater from intruding into the subsurface. Economic benefits include lower maintenance costs and water savings. These benefits must be balanced against potential environmental concerns. Rainwater passing through the artificial turf may leach contaminants from the crumb rubber contained in the infill.

ES-2 Scope and Limitations of Study

The investigative approach consisted of coordinated laboratory, pilot, and field experiments, and thermodynamic modeling. Two small (12.6 sqft) pilot systems were built using commercial artificial turf and rock materials to study the leachate production under natural rainfall conditions. Field experiments on an existing sports field were conducted at a local college. The factors that govern leachate production were studied in the laboratory under controlled conditions in bench-scale leaching tests. The pilot setups were equipped with samplers at different depths to study contaminant behavior during the percolation of leachate produced during natural rainfall. A methodology was developed to investigate the metal, TOC and PAH content in leachate from artificial turf sports fields and to determine contaminant attenuation in the supporting rock layer. Two leachate-sampling systems were installed at the field site. Leachate was collected immediately below the artificial turf layer and in the rock bed at different depths. Leachate collected during a rain event was withdrawn and analyzed. The metal contents

of crumb rubber, fiber blades, and geotextiles were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Crumb rubber was characterized using electron microprobe analysis (EMPA). The geochemistry controlling the concentration of Zn was evaluated using thermodynamic modeling.

ES-3 Project Goals and Outcomes

The purpose of this study was to determine whether metals, polynuclear aromatic hydrocarbon compounds (PAHs), and total (aggregate) organic carbon are leached by rainwater from artificial turf fields.

Objective 1: Characterize the source of heavy metals in artificial turf and quantify their leaching rates under controlled experimental conditions (e.g., temperature and sunlight exposure).

In fresh crumb rubber samples, zinc oxide, elemental iron, and titanium oxide particles were detected. The most abundant metal present was Zn (20 mg/g). Co, Fe, Mo, Pb, Sn, and Ti were present at levels averaging approximately 0.01mg/g to 1mg/g; Ba, Cr, Mn, Ni and Sr were detected below 0.01 mg/g. Fiber blade material was found to contain significant quantities of Al and Fe, and the carpet backing contained mainly Ca (7-9%) and Mg (0.3-1.3%). Metal contents in crumb rubber from different manufacturers generally showed the same metal profile with Zn being the major heavy metal component in all cases.

In the batch leachate experiments with crumb rubber, Zn was the only heavy metal detected at significant concentrations, and subsequent laboratory studies focused on Zn. Batch experiments indicated continuous soaking by purified laboratory water (Milli-Q water) and synthetic rainwater (at pH 5.5-5.6) leached approximately the same amounts of Zn (5% in 416 days). Lowering pH to 3.4-3.5 increased leaching by approximately 50%.

Laboratory columns packed with crumb rubber leach Zn into the water passing through the column at rates that slowly decrease with time. When the flow is stopped, Zn

continues to leach into the stagnant pore water, leading to a Zn spike when flow resumes. Heat and sunlight were shown to promote Zn mobilization. Carbonaceous rock materials strongly adsorb and retain Zn contained in leachate.

Objective 2: Determine the leaching rates of heavy metals and organic contaminants under field conditions.

Pilot experiments were consistent with laboratory observations. Pauses between rain events produced pulses of leachate with high Zn concentrations; in pilot experiments concentrations ranged from 0.8 to 2.8 mg/L. The Zn concentrations in leachate produced by rainfall events depended on quantity, intensity, duration, and the time between rain events. Rock materials were found to attenuate Zn contained in leachate. Zn concentrations decreased to below 0.006 mg/L after percolating through the rock bed. Concentrations at the outflow of the bed remained low during the entire 2007-2008 rainy season, suggesting that exhausting its Zn retention capacity will take more than one season. The concentrations of Ba, Co, Fe, Mn, Ni, and Sr were at or close to the instrumental detection limit and were not further investigated.

During field-testing, concentrations of Zn in the leachate ranged from 0.13 to 0.47 mg/L, and Zn was the major metal in leachate samples (approximately 100 times higher than all other heavy metals). The other metals tested were present at concentrations near 0.005 mg/L or below. The observed Zn concentrations varied over time, likely because heat and sunlight promoted Zn release. Initial Zn concentrations after dry periods were high, but decreased with subsequent rain events. Such behavior is consistent with decreasing Zn mobilization with shorter drying, warming, and irradiation intervals. Zn concentrations exceeding 5 mg/L (EPA secondary maximum contaminant limit) were not observed under field conditions.

TOC released from artificial turf ranged from approximately 7 to 15 mg/L, which is comparable to other sources of urban runoff. Passage through the rock bed did not attenuate TOC significantly, perhaps because there were unfavorable conditions for sorption and biodegradation. The composition of TOC and its long-term leaching behavior was not further investigated. Leachate from one pilot setup (TURF B) was

analyzed for the 16 EPA-regulated PAHs, potential contaminants of concern. The total concentrations of the PAHs varied between 0.3 and 0.7 μg/L. Overall, these results suggest that the potential for artificial turf to leach PAHs into water is quite low.

Objective 3: Quantify the sorption of heavy metals and organic contaminants in artificial turf leachate on representative field materials to assess the risk of leachate components reaching the groundwater table.

Artificial turf fields are engineered to prevent the field runoff from entering the subsurface. Contaminants leached from artificial turf sites are discharged to storm sewers and may ultimately impact surface water ecosystems.

ES-4 Recommendations

1) The sustainability of Zn attenuation by the underlying rock material should be verified in long-term experiments. Leachate concentrations below the rock material layer should be monitored for 5 years or longer, if possible, during the entire lifetime cycle of the artificial turf field to determine whether breakthrough of Zn occurs.

2) The mechanism of Zn (and other heavy metals) retention on the rock material should be identified to predict the breakthrough behavior or retention capacity.

3) Conditions under which Zn retained by a rock layer is mobilized should be studied. This would help ascertain whether sorption/precipitation of Zn onto these materials represents a long-term protection against Zn release.

4) Environmental implications of disposal of spent bedrock saturated with Zn should be evaluated.

5) Potential impacts of artificial turf leachate on surface water ecosystems should be further assessed.

6) This study focused on aquatic impacts. Other impacts, e.g., release of volatiles and particulate matter into the air should be considered.

1. INTRODUCTION

1.1. Artificial Turf as an Alternative to Natural Lawns

Artificial turf is a grass-like surfacing material constructed from single-filament synthetic fibers attached to plastic sheets. The fibers are embedded in a layer of granular padding (infill) containing crumb rubber produced from waste rubber products. Artificial turf is typically used in areas where growing natural grass is difficult and where maintaining a lawn is expensive, such as in some sports fields, indoor arenas, and playgrounds. One of the greatest benefits of artificial turf is water savings. In the Pacific Northwest, a typical sand-based soccer/football field uses between 2.5 million and 3.5 million gallons of water per year (Sweet and Evans, 2002). In the Bay Area, irrigation of a 5.4 acre-football practice field consumes on average 5.8 million gallons of water per year (Stanford University, 2003). In contrast, artificial turf fields require no irrigation (although water may occasionally be used for cleaning and cooling). Other significant benefits of artificial turf are lower maintenance costs: mowing, fertilizing, use of herbicides and re-seeding are not required.

Most brands of artificial turf being installed today are composed of three layers: (a) artificial grass fibers (a polyethylene or polyethylene blend); (b) infill (particulate rubber from one or more sources, or a mixture of sand and rubber particles); and (c) a carpet backing (a blend of polypropylene, polyamide 6, polyolefins, and/or polyurethane) that supports the grass fibers. The main sources of particulate rubber infill (rubber crumbs) are used tires, recycled tennis shoes, and rubber manufactured specifically for infill purposes. Artificial turf fields are installed on top of a bed of crushed rocks and a drainage system that typically feeds the runoff to storm sewers or surface waterways. One or more geotextiles are placed above the compacted clay layer and within artificial

turf field, which allows removal the artificial turf or parts of the artificial turf after its lifetime.

During percolation through the artificial turf, rainwater can leach soluble components from the infill materials. Here, runoff that has contacted infill material is termed “leachate”. The environmental concerns associated with the use of artificial turf stems primarily from the infilled crumb rubber; significant impacts of the other components, i.e., plastic grass fiber, and carpet backing, are unknown. The most popular infill is prepared from spent automobile tires by grinding and/or cryogenic shattering. Grinding tire materials into small crumbs creates a large area of fresh rubber surfaces, thereby enhancing the leaching potential for tire components. The following two sections focus on the water quality and ecotoxicological impacts of leachate from tire rubber.

1.2. Water Quality Impacts of Artificial Turf

1.2.1. Components of Tire Rubber

Tire rubber typically consists of natural or synthetic rubber and numerous ingredients added to achieve the desired properties of tires, such as strength and photochemical stability. Additives include sulfur compounds, silica, phenolic resins, aromatic, naphthenic or paraffinic oils, petroleum waxes, zinc oxide, titanium dioxide, carbon black, fatty acids, nylon, polyester, or other fabric, inert materials or stainless steel. Zinc oxide is added during rubber manufacturing as a vulcanizing agent. On average, the zinc oxide (ZnO) content in the tread of car and truck tires is 0.96% and 1.7% (i.e., 0.78% and 1.4% of Zn), respectively (BLIC, Liaison Office of the Rubber Industry of the E.U., 2001 zinc survey data).

Cadmium may be expected to be present in waste tires because it is an impurity of zinc or it is absorbed from road surfaces during use. (Cadmium is a trace component of diesel fuel, gasoline, and lubricating oil.) The U.S. Bureau of Standards’ standard zinc slab has 0.53% cadmium, and impure zinc can contain up to 2% cadmium (Schroeder,

1974). Iron may be present because residues of steel belts are shredded along with the rubber.

1.2.2. Water Quality Impacts of Tire Materials

The environmental impacts of metals and organic additives that may leach from tire materials (e.g., Zn, Cd, Cr, Co, Fe, and Mn) have been studied widely, and considerable data have been accumulated about water quality and ecological impacts, as summarized in the following paragraphs. Heavy metals that have been detected in tire leachate include zinc, aluminum, cadmium, chromium, copper, iron, magnesium, manganese, and molybdenum (Chalker-Scott, 2005.) The organic compounds found in rubber leachate result from the breakdown of the organic building blocks of rubber, various plasticizers, and accelerators used during the vulcanizing process (Chalker-Scott, 2005).

In a field study that investigated effects of tires on water quality (Humphrey and Katz, 2001), tire shreds were placed into a trench that was dug to below the water table. The Humphrey and Katz study concluded that tire shreds had negligible effects on the concentrations of the metals with defined *primary* drinking water standards (antimony, arsenic, barium, beryllium, cadmium, chromium, copper). However, the study reported elevated concentrations of iron, manganese, and zinc, which are regulated as *secondary* drinking contaminants. Of those, iron and manganese were probably of geochemical origin (i.e., released from the soil under reducing conditions caused be tire leachate) whereas zinc most likely originated from the tire material. The concentrations of iron, manganese, and zinc decreased to near background levels 0.6 to 3 meters downgradient of the tire shred filled trench, indicating strong attenuation by the soil. Trace concentrations of organic contaminants, including benzene, xylenes, toluene, 2-butanone, 4-methyl-2-prentanone, aniline, phenol, *m*- and *p*-cresol, and benzoic acid, were also found, and probably originated from the degradation of the rubber matrix. As for the metals, these compounds were strongly attenuated over a short distance and their concentrations were below detection limits in the downgradient wells (Humphrey and Katz, 2001).

In a survey of eight laboratory and field studies conducted on scrap tires, iron levels consistently exceeded the recommended allowable level (Liu et al, 1998). Conflicting results have been reported for other heavy metals (e.g., cadmium, barium, manganese) and organic contaminants (petroleum hydrocarbons, polynuclear aromatic hydrocarbons (PAH), volatiles, and semi-volatiles), which might have been caused by the differences in soil mineralogy, water infiltration rate, and pH (Liu et al, 1998).

1.3. Ecotoxicological Studies

Limited information is available on the ecotoxicity of tire leachate. The environmental impact of metal leaching from rubber tires has to be evaluated considering that trace amounts of some heavy metals are required by living organisms. However, when present in excess amounts, they can be detrimental to the organisms (Berti et al., 1996). Nonessential heavy metals, such as arsenic, antimony, cadmium, chromium, mercury, and lead, are of particular concern as surface water and soil pollutants (Kennish, 1992). A potential contaminant of concern in leachate is lead because of its toxicity to humans, especially children. However, lead is not used in the manufacturing of rubber or tires. Potentially, lead may stem from impure components or uptake from lead-contaminated roads.

Relatively high concentrations of zinc (approximately 0.025 mg/L), and up to 62 specific organic contaminants (mostly arylamines and phenols) were found in leachate of automobile tires (Abernethy, 1994). These authors observed that leachate exhibited toxicity to fish (rainbow trout) and that activated carbon adsorption removed toxicity. Exposure to sunlight reduced the toxicity slightly, while aeration, addition of acid, base, antioxidant, and a metal chelating agent had no effect on toxicity (Abernethy, 1994). Nelson et al. (1994) analyzed tire leachate and detected zinc at potentially toxic levels, and cadmium, copper, and lead at levels significantly above background, but no specific organic compounds. A recent *in vitro* and *in vivo* toxicity study showed that zinc leaching out of tire debris can accumulate in and affect African clawed frog (*X. laevis)* embryos (Gualtieri et al., 2005). The same study demonstrated that the organic compounds extracted from tire debris were toxic to A549 cells (a cell line derived from a human lung

carcinoma) and affected cell morphology, cell proliferation and DNA, and produced severe malformations in developing *X. laevis* embryos.

Zinc exerts phytotoxicity by interfering with chlorophyll biosynthesis and with the uptake, translocation, and/or utilization of iron, an essential nutrient (Chaney, 1993). Although zinc is essential for plant growth, decline in plant growth that is directly attributable to zinc toxicity has been found in growth media containing tire rubber (Schulz 1987; Bowman et al., 1994; Handreck, 1996). Other heavy metals can cause stress and toxic effects in plants when present at sufficiently high levels (Prasad and Hagemeyer, 1999). For example, cadmium can permeate through calcium channels and disturb plant water status, leading to plant wilting (Perfus-Barbeoch et al., 2002).

1.4. Speciation of Heavy Metals in Water and Soil

In surface waters, heavy metals are distributed between colloidal, particulate, or aqueous phases depending on the affinity of the metal for the solid phases present. Typically, the dissolved concentrations are low because heavy metals adsorb strongly on hydroxides, oxides, silicates, or sulfides, clay minerals, silica, and organic matter (Kennish, 1992; Elliot et al., 1986; Connell and Mill, 1984; Huang and Blankenship, 1989). Under neutral to slightly basic conditions, which are typical of most soils, cationic metals are strongly adsorbed on the clay fractions and can be adsorbed by hydrous oxides of iron, aluminum, or manganese present in soil minerals (Ghosh and Singh, 2005; Ghosh and Singh, 2005; Basta et al., 1993). On the other hand, adsorption of heavy metals can be reduced in the presence of elevated salt concentrations due to increased competition between cations and heavy metals (Benjamin and Leckie, 1980).

1.5. Motivation for Study

Taken together, the above information suggests that release of heavy metals from rubber used as infill in artificial turf is a potential environmental concern. Although artificial turf was first introduced in the 1960s, the potential environmental impact of

heavy metals and organic contaminants leaching from artificial turf has received little attention in the peer-reviewed literature, and available information appears inconsistent.

An exploratory study commissioned by Santa Clara Valley Water District (SCVWD) found heavy metals (barium, chromium, copper, and particularly, zinc) and organic compounds (benzoic acid and phenol) leaching from two artificial turfs (from two different manufacturers) using the Toxicity Characteristic Leaching Procedure (TCLP). Benzoic acid and phenol are deemed of lesser concern because they can be photochemically or biologically degraded (Hecht et al. 2000). Thus, in surface and groundwater relatively effective natural attenuation of these contaminants can be expected. Results of the TCLP study are difficult to extrapolate to environmental conditions because conditions were far more aggressive than those encountered in the environment.

1.6. Investigative Approach

1.6.1. General

This study was initiated in mid-2006 and lasted through summer 2008. The investigative approach consisted of coordinated bench- (laboratory), pilot-, and field-scale experiments. Data collected at actual field sites are most relevant from a regulatory and public perception viewpoint. Field data were collected at the field site beginning 01/23/08. Laboratory batch and column studies were conducted to simulate contaminant release and transport under controlled conditions and to evaluate the effect of environmental factors (rainfall volume, heat and light) to study. Two pilot systems were constructed, one in-house by Stanford using TURF C components and one by an artificial turf manufacturer (TURF B). TURF C was designed to represent a local site. The pilot systems (pilots) were equipped with sampling devices and installed outside at the Stanford campus.

1.6.2. Factors controlling leachate production and contaminant release

The volume of leachate production is controlled by the intensity, duration and frequency of rainfall events. Precipitation in the Bay Area is highly irregular and sampling rainwater and leachate sampling is unpredictable. The 2006/7-period was relatively dry and yielded limited data. By contrast, during the 2007/8-period heavy rainstorms flooded sampling systems on several occasions.

Environmental factors such as temperature, sunlight, and rainwater pH may affect contaminant leaching from rubber crumbs. Because rubber particles are black, they are excellent traps for light and thermal radiation. On a sunny afternoon in July 2006, the temperature at the surface of an artificial turf field was 64°C, 36°C higher than the ambient air temperature (28°C). By comparison, the surface temperature of a nearby grass turf was only 34°C, while that of bare ground was 52°C. Crumb rubber particles were exposed to heat and light in the laboratory and the impact on leaching was evaluated using column tests. Rainwater pH can vary with air quality and affect metal mobility. Crumb rubber was leached by synthetic rainwater at pH 5.5-5.6 and pH 3.4-3.5 to study pH effects. Zn speciation in leachate was evaluated using the geochemical modeling program MINTEQ (released by EPA in 1999). The retention capacity of rock bed material for Zn was studied using laboratory columns by passing an aqueous Zn solution through the columns at a steady rate and monitoring Zn in the column effluent.

2. OBJECTIVES

The overall objective of this study was to evaluate the potential of leachate from artificial turf fields impacting the quality of surface water and groundwater. The investigative approach of the second year focused on the release of Zn, polynuclear aromatic hydrocarbon compounds (PAHs), and total (aggregate) organic carbon (TOC). The specific objectives included:

1) Characterize the source of heavy metals in artificial turf and quantify their leaching rates under controlled experimental conditions (e.g., temperature and sunlight exposure),

2) Determine the leaching rates of heavy metals and organic contaminants under field conditions,

3) Quantify the sorption of heavy metals and organic contaminants in artificial turf leachate on representative field materials to assess the potential of leachate components reaching groundwater table.

3. EXPERIMENTAL METHODS

3.1. Sampling and Analytical Methods

The chemical parameters investigated in this study are summarized in Table 1.

Table 1. Summary of inorganic and organic parameters analyzed

Inorganic species	Organic parameters
Zn, Fe, Cd, Co, Cr, Cu, Mn, Ni, Pb, Ag, Al, As, Ba, Be, Ca, K, Mg, Mo, Na, Sb, Se, Sn, Sr, Ti, Tl, and V	Total organic carbon (TOC), Total polycyclic aromatic hydrocarbon (PAH)

The leachate samples collected from the pilot setups and field site were collected in glass (for organic analysis) and plastic (for heavy metal analysis) bottles and immediately transported back to the laboratory. The total volumes of the samples (with accuracy of ±10 mL), date and time, and location were recorded.

3.1.1. Heavy Metals

Sub-samples for metal analysis were filtered using 0.45 μm syringe filters, acidified by HNO3, and stored at 4°C until analysis. Heavy metal contents were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a TJA IRIS Advantage/1000 Radial ICAP Spectrometer. Water purified with a Milli-Q system (Millipore Corp. Billerica, MA 01821) (referred to as Milli-Q water) and high-purity nitric acid (TraceMetal-grade, Fisher Scientific, Pittsburgh, PA) were used for the preparation of all standard solutions.

Calibration solutions (0.005, 0.01, 0.1, and 1 mg/L) for 24 elements (Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, and V) were prepared by appropriate dilution of a 100 mg/L multi-element stock standard solution (instrument calibration standard 2, Spex Certiprep, Metuchen, NJ) with 0.5% (v/v) nitric acid. The Fe and Zn, concentrations in the calibration standards were a factor of 16 higher. Appropriate concentrations were obtained by adding 1000 mg/L single-element solution standards (Spex Certiprep, Metuchen, NJ). The ICP-AES was calibrated for each batch of samples. A standard solution containing 1.6 mg Fe and Zn and 0.1 mg/L of all other elements was analyzed as an instrument check standard once every 15 samples. Milli-Q water and standard solutions were also inserted as control samples for ICP-AES measurements. The detection limits for these elements ranged from 0.005 to 0.01 mg/L. Although a total of 26 elements were simultaneously measured in the ICP-AES analysis, greater attention was paid to Zn, Fe, Cd, Co, Cr, Cu, Mn, Ni, and Pb.

3.1.2. Total Organic Carbon (TOC)

Sub-samples for total organic carbon (TOC) analysis were centrifuged, and the supernatants were acidified by adding dilute HCl and stored at 4°C until analysis (Liu et al., 2004). For TOC analysis, a Shimadzu TOC-5000A instrument was used. The method is based on decomposing the organic carbon to CO_2 at 680°C in a column filled with oxidation catalyst and detection of the liberated CO_2 with a non-dispersive infrared gas analyzer.

3.1.3. Polycyclic aromatic hydrocarbons (PAHs)

PAH extraction from rainwater and artificial turf leachate samples was done according to EPA Method 610. After filtration, one-liter samples were solvent extracted with hexane using a separatory funnel. Following three sequential extractions, the extracts were combined, concentrated, and reconstituted in cyclohexane. Cleanup was performed on the final extract using a silica gel column as outlined in EPA Method 3630C. A gas chromatograph (Agilent Model 6890) equipped with a fused silica capillary

column (HP-5, 30 m × 0.25 mm i.d.) and a flame ionization detector (FID) was used for analysis based on EPA Method 8100 for PAHs. 2-Fluorobiphenyl was added to the extract at the level of 2.0 mg/L as the internal standard. A standard mixture of the 16 EPA priority pollutant PAHs obtained from Ultra Scientific Inc. (North Kingstown, RI) was used for calibration (Hong et al., 2003).

3.1.4. Quality Assurance/Quality Control

For Quality Assurance/Quality Control (QA/QC), we used deionized water and standard solutions as control samples in ICP-AES and TOC measurements. Ashing and leaching experiments for crumb rubber were executed in triplicate. A blank tube and filter paper were used as a control in laboratory leaching and high temperature ashing experiments. Soil water from a regularly irrigated grass meadow and rainwater were also used as control samples. Measurements were generally carried out with multiple replicates. The mean and standard deviation and 99% confidence intervals (CIs) were calculated using standard procedures.

3.2. Geochemical Modeling

The chemical speciation of Zn in artificial turf leachate was calculated using the chemical equilibrium model Visual MINTEQ (version 2.53). The aqueous composition was based on data reported by Hem (1985) for Menlo Park (CA) rainwater: Ca^{2+} 0.8 mg/L; Mg^{2+} 1.2 mg/L; Na^{+} 9.4 mg/L; HCO_3^{-} 4 mg/L; SO_4^{2-} 7.6 mg/L; Cl^{-} 17 mg/L; pH 5.5. Visual MINTEQ (version 2.53) is a Windows version of MINTEQA2 (version 4.0) released by the US EPA in 1999. MINTEQ employs a chemical equilibrium model to calculate metal speciation and solubility equilibria in natural aqueous systems. The equilibrium constants used for ion speciation are based on the MINTEQA2 database, which has been updated using the most recent NIST data for >3000 aqueous species and >600 solids. The extended Debye-Hückel equation was used to estimate individual ion activity coefficients (valid for ionic strengths up to approximately 0.7-0.8 mol/L).

For the speciation of Zn in homogenous aqueous solutions, i.e., in the absence of a solid phase, three types of systems were modeled: a carbonate-free system, a closed system with dissolved carbonate species, and an open system in equilibrium with atmospheric CO_2 (partial pressure: $10^{-3.42}$ atm.). To study the influence of anion concentrations on Zn speciation, the concentrations of Cl^- and SO_4^{2-} were increased to 10 and 100 times of the concentrations in rainwater in certain runs. Geochemical behavior of Zn was simulated for Zn concentrations of 1.6 mg/L (a typical value found in leachate samples) and 16 mg/L. Chemical speciation of Zn in the absence of solid phases was calculated between pH 0 and 14. The speciation diagrams are shown in Appendix A. For Zn speciation in the presence of solid phases, we considered an open system in equilibrium with atmospheric CO_2 (partial pressure: $10^{-3.42}$ atm.) and calcite ($CaCO_3$) as the infinite solid phase. As potential Zn-precipitate, we specified a finite quantity (10 mol/L) of hydrozincite ($Zn_5(OH)_6(CO_3)_{2(s)}$) or smithsonite ($ZnCO_{3(s)}$). In the presence of calcite, the chemical speciation of Zn was calculated between pH 5.5 and 10.0.

3.3. Characterization of Artificial Turf Components

3.3.1. Materials

Laboratory studies focused on two major brands of artificial turf (Turf A and Turf B). Two samples were obtained from each of the two major artificial turf manufacturers. TURF A products contain 100% rubber infill, while TURF B products are filled with an approximately half/half mixture of rubber and sand. Samples each were obtained directly from the respective manufacturers. Sub-samples of infill material, fiber blade, and carpet-backing were characterized with respect to heavy metal contents and leaching characteristics using the methods described below.

3.3.2. Electron microprobe analysis (EMPA)

The rubber crumb particles from artificial turf were examined for the presence of heavy metal particles and their distribution inside the crumb rubber using EMPA.

Scanning electron micrographs and X-ray spectra were obtained with a JEOL Superprobe (Model JXA-733A) operated at 15 KV and 15 nA.

3.3.3. High temperature ashing and heavy metal analysis

The total amounts of heavy metals present in different components of artificial turf were quantified through ashing followed by ICP-AES analysis. Artificial turf was separated into fiber blade, infill materials, and carpet backing. The crumb rubber of TURF B was gravimetrically separated from sand through floatation in water. The procedure was repeated three times. Rubber particulates attached to the fiber blade and carpet backing were removed by washing (five times) with rapidly flowing Milli-Q water. The washed materials were dried at 50°C for 1 h. Samples of 1.00 g of fiber blade, crumb rubber, or carpet backing were weighted into porcelain crucibles and ashed at 550°C overnight. The residues were dissolved by nitric acid and analyzed for heavy metals by ICP-AES.

3.3.4. Calcium carbonate content in rock materials

For constructing the TURF C pilot setup, the top and bottom rock materials from the athletic field of a local high school (MH) were used. The materials were visually identified as shale. Fine shale is a fine-grained sedimentary rock whose original constituents were clay minerals. The top rock material supplied with the TURF B pilot setup appeared to be mudstone, a fine-grained sedimentary rock geologically formed from mud. The bottom rock material supplied with the TURF B pilot setup was composed of river pebbles.

The rock materials of the TURF C pilot and the TURF B pilot setup were tested for calcium carbonate ($CaCO_3$) by adding hydrochloric acid. The TURF C and the upper layer of the TURF B reacted vigorously releasing gas indicating the presence of $CaCO_3$. By contrast, the bottom rock from the TURF B pilot setup showed much lower reactivity with HCl.

The calcium carbonate content in these rock materials analyzed using the "Loss-on-Ignition" method. First, the rock materials were heated at 105°C for 3 hours to remove physisorbed water and then weighted. After that, they were heated to above 900 °C in a muffle furnace for >3 hours. The final weights of the rock materials were recorded after cooling to room temperature. The calcium carbonate content was calculated from the weight loss (for the reaction $CaCO_3 \rightarrow CaO + CO_2$) assuming that calcium carbonate was the only carbonate mineral present.

3.4. Laboratory Leaching Studies

3.4.1. Batch experiments

Batch experiments were conducted to study contaminant release from different artificial turf components into three different media: Milli-Q water, artificial rainwater, and acidic artificial rainwater. Milli-Q water was used to study leaching of heavy metals in the absence of ionic species. Leaching by synthetic rainwater and acid rainwater was studied to evaluate contaminant release under natural conditions and the influence of pH.

The experimental design of batch leaching experiments is depicted in Figures 1 and 2. To 50-mL graduated polypropylene tubes containing the 1g solid samples (fiber blade, infill materials, or carpet backing) were added 40 mL of liquid medium. The vials were capped and placed on a table shaker operated at a rate of 200 rpm at room temperature. Liquid samples were obtained by completely withdrawing the solution from the vial using a disposable polypropylene/polyethylene syringe equipped with a 0.45 μm cellulose acetate syringe filter. The filtered solution was transferred to sample vials. The leaching experiment was repeated to evaluate the leaching capacity.

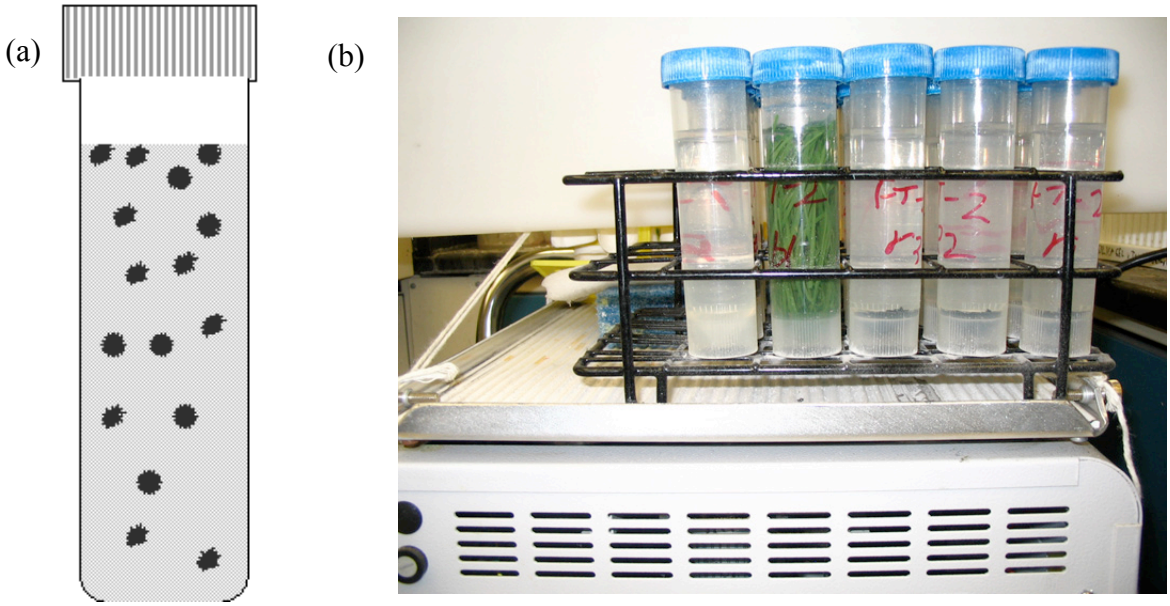


Figure 1. Experimental setup for leaching of heavy metals from artificial turf components: (a) schematic of a sample tube; (b) view of sample tubes mounted on a shaking table.

The media were prepared as follows: Milli-Q with a resistivity of greater than 18.2 MΩ cm (megaohm-centimeter) at 25°C. Synthetic rainwater was prepared with Milli-Q water and contained 190 μM NaCl, 20 μM $CaCl_2$, 50 μM $MgCl_2$, 80 μM Na_2SO_4, and 60 μM $NaHCO_3$, based on the chemical makeup of rainfall in Menlo Park, CA (Hem, 1985). The pH was adjusted by HCl solution to 5.5-5.6, typical of natural rainwater.

Synthetic acid rainwater was prepared with the same formula as the synthetic rainwater, except that the final solution pH was adjusted to 3.4-3.5 with HNO_3. The synthetic acid rainwater was used to represent the case of acid rain, which usually results from elevated levels of nitric and sulfuric acids caused by air pollution.

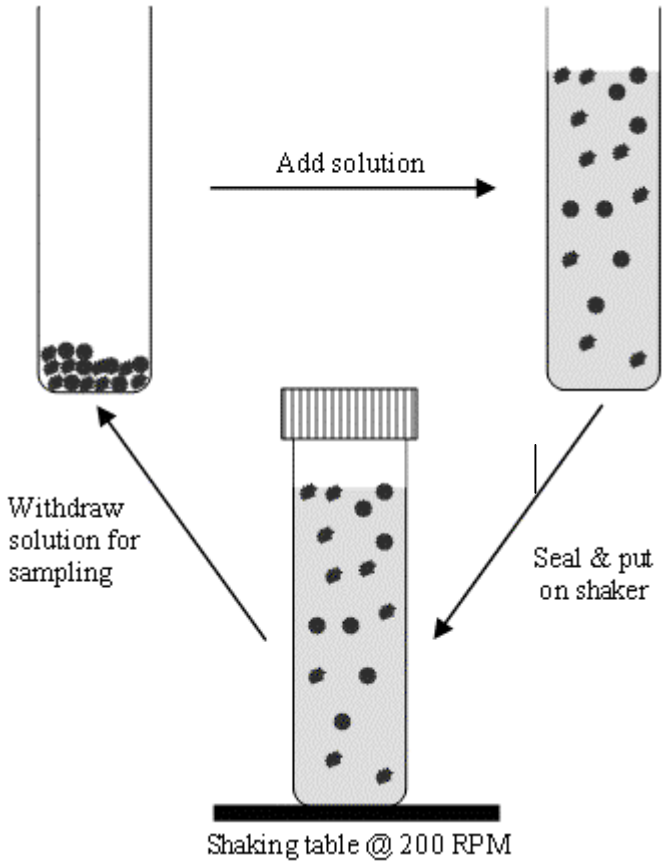


Figure 2. Schematic illustration for the sequential batch procedures for experimental sampling of heavy metals from ground rubber.

Further leaching experiments in synthetic rainwater and synthetic acid rain were only conducted with crumb rubber. The crumb rubber samples were separated from fresh artificial turf samples supplied by the manufacturers, and from used crumb rubber from three local artificial turf fields (GI, GR, and OG).

3.4.2. Column leaching tests

To test the release of metals into fresh medium from rubber crumb samples, a "column leach test" was developed as follows: a glass column (100 mm long and 25 mm in diameter) was packed with 12 g crumb rubber while gently tapping the column to achieve uniform packing. The resulting layer was 4.0 cm high, which is within the typical range of the thickness of infill layer (2.5 to 5 cm or 1 to 2 inches). A high-performance

liquid chromatography (HPLC) pump was used to feed synthetic rainwater at a constant rate to the top of the column, as shown in Figure 3. Leaching tests lasted for 48 to 100 min. The flow rate was 0.45 or 0.90 mL/min, corresponding to rainfall intensities of 2.17 and 4.33 inch/hour, respectively. The feed water dripped from the column inlet onto the top of the packing and percolated through the rubber layer. Complete water saturation occurred after feeding 10-15 mL to the column. Leachate samples (>4.5 mL per sample) were collected in glass sample vials at intervals of 5 to 15 min. At the end of the leaching experiment, the column was allowed to drain for approximately 22 h before initiating another experiment.

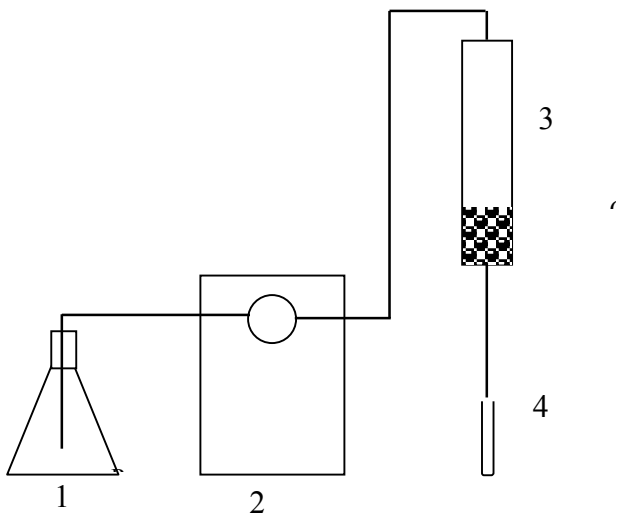


Figure 3. Schematic illustration of the column leaching setup: 1: reservoir; 2: pump; 3: column; 4: sampling vial.

3.4.3. Influence of sunlight and temperature on leaching of zinc

To study the combined impact of sunlight and heat on the release of zinc, rubber particles obtained from GR site were irradiated after being exposed to artificial sunlight, heat or both. Artificial sunlight was produced in an Atlas Suntest CPS+ photosimulator (Chicago, IL) equipped with a 1.1 kW xenon arc lamp and glass filters blocking the

transmission of wavelengths below 290 nm. The filter is transparent for wavelengths from 290 nm to 800 nm. The light intensity was 765 W/m^2, which is equivalent to mid-day, mid-summer sun in California (Lin and Reinhard, 2005). The light intensity was verified previously (Plumlee and Reinhard, 2007). Rubber particles were transferred from the column into a glass beaker (2.5 cm in diameter) and irradiated for 22 hr or longer. Following irradiation, particles were packed into the column and tested for leaching using the column test described in Section 4.4.2.

The impact of a hot day on Zn leaching was studied as follows: samples of crumb rubber were exposed to sunlight, high temperature (55°C), and sunlight and high temperature combined. After exposure, rubber samples were cooled to room temperature (24±1°C), subjected to the column leach tests described in section 4.4.2.

3.4.4. Heavy metal sorption and desorption on crushed rock

The fine rock material obtained from the HM field was packed into a glass column 25 mm in diameter and 100 mm in length by gently hand tapping the column to achieve tight packing. The thickness of the rock layer in the column was 4.0 inches, which is the typical thickness of the fine rock material used in artificial turf fields. The total rock mass in the column was 73.4 g.

A synthetic leachate was prepared containing the following elements: 1.0 mg/L Zn and 0.05 mg/L Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, and V. The solution was obtained by appropriately diluting a 100 mg/L multi-element stock standard solution (instrument calibration standard 2, Spex Certiprep, Metuchen, NJ) and a 1000 mg/L single-element solution standard for Zn (Spex Certiprep, Metuchen, NJ) with synthetic rainwater. The final pH of the synthetic leachate was adjusted to 5.6 with 0.1 mol/L NaOH solution.

A high-performance liquid chromatography (HPLC) pump fed the synthetic leachate to the column at a rate of 0.45 mL/min (same as column leach test). Loading (sorption) of the column continued for 36 hours. During this time, column effluent

samples were collected in glass vials every 10 min using an automated fraction collector. Then the leaching behavior of the metals retained in the column was examined by flushing the column for 82 hours with synthetic rainwater at a rate of 0.45 mL/min.

3.5. Design of Pilot Systems

3.5.1. TURF C pilot set up

The pilot constructed by Stanford was constructed to reproduce conditions at the MH site. Materials used were obtained from site MH, which was under construction at the time. The artificial turf used is designated as TURF C. The TURF C pilot consisted of a circular high-density polyethylene (HDPE) tank filled in sequence with layers of sand (5 in), native soil (4.5 in), base rock (5 in), top rock (4 in), and artificial turf (2 in), as indicated in Figure 4a. Hereafter, this set is referred to as "TURF C pilot." Sampling pans were installed below different layers for sampling leachate at specific depths as shown in Figure 4b. Rainwater was collected using the setup shown in Figure 4c. The rainwater sampler was placed near the pilot system. For sampling leachate from the artificial turf layer, a separate sampler was built using a sampling pan that contained a layer of artificial turf (Figure 4d). This ampler was placed next to the tank. Geotextile sheets separated different layers, as indicated in Figure 4a. At artificial turf fields, geotextile is installed between the rock layer and the base soil to recover materials at the end of their lifetime. Geotextile is readily permeable to avoid impact on drainage. Geotextile is typically made from relatively inert materials such as polypropylene or polyester, and is not expected to interact significantly with metal species. The geotextile used in TURF C was also obtained from site MH. It was in needle punched form, dark grey, and was about 2-3 mm thick. In the TURF C pilot, geotextile was used to prevent rubber and rock particles from being transported into the sampling pans.

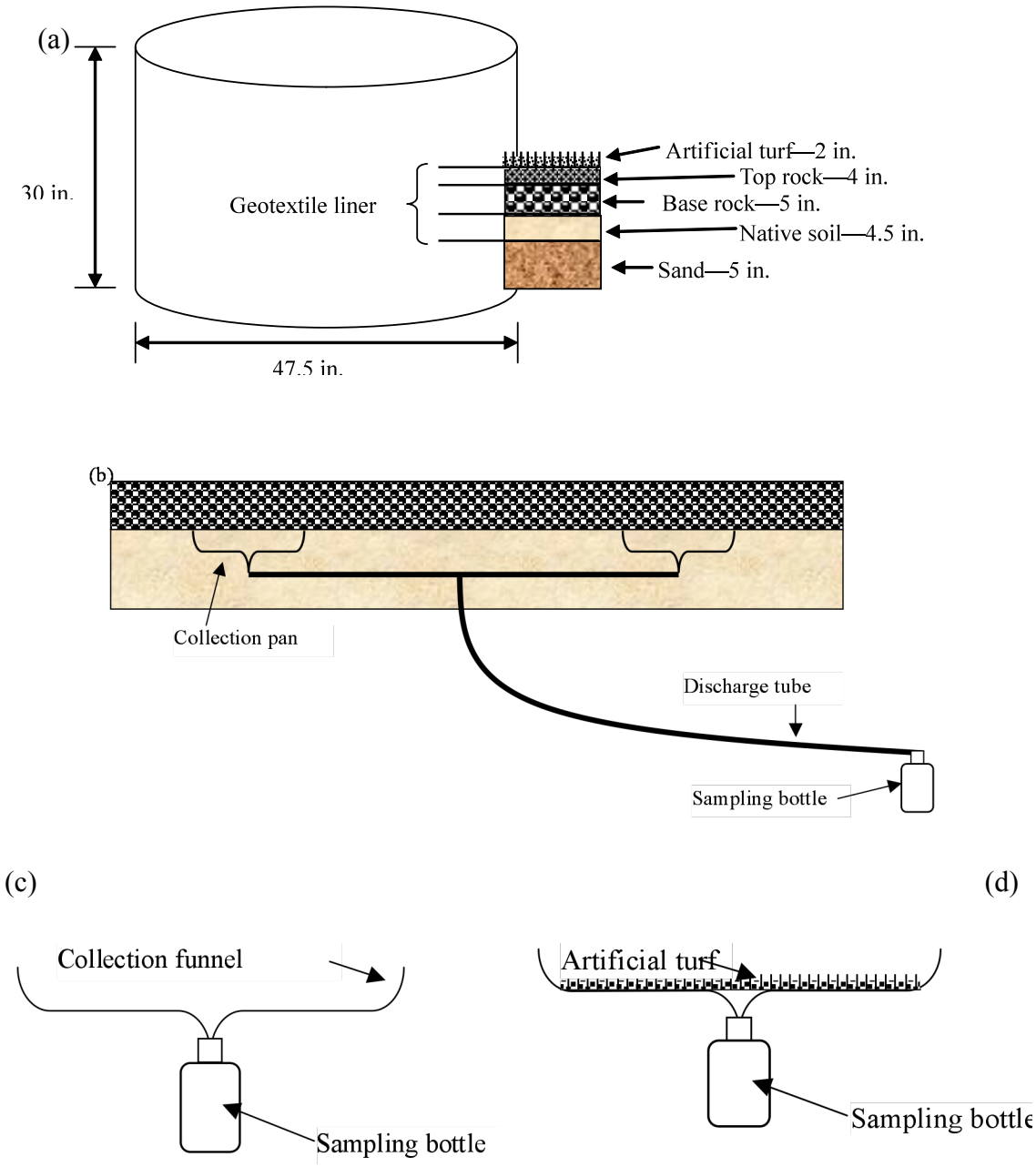


Figure 4. TURF C pilot artificial turf setup: (a) overview of design: tank containing sand, native soil, base rock , top rock, and artificial turf, layers of porous geotextile between layers prevent mixing of materials; (b) illustration of the built-in sampling system; (c) rainwater collection setup; (d) artificial turf sampler consisting of sampling pan containing artificial turf layer and sample bottle. The artificial turf sampler was set up next to the tank.

3.5.2. TURF B pilot setup

A second pilot was constructed by the manufacturer of TURF B and delivered to Stanford on 11/28/0. This pilot was square-shaped with a side length of 35.5 inches. The TURF B pilot was modified to allow for sampling below the artificial turf layer and the base rock layer, as depicted in Figure 5. Leachate was transferred to a sample bottle by suction with a battery-operated pump. Rocks below the artificial turf layer were removed and a 2 in-deep plastic sampling pan (12×10 in) was installed. A hole was drilled into the bottom of the Plexiglas tank and connected to a sampling bottle with a ½-in plastic tube. Installation of the sampling system on this setup (Figure 5) was finished on 12/19/07. It was similar to the TURF C pilot except that only two layers were sampled.

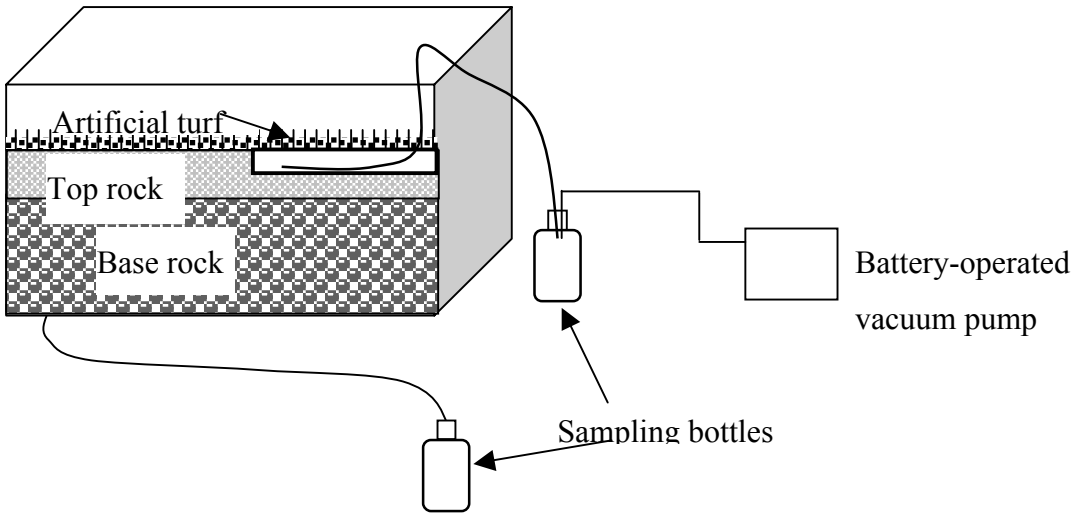


Figure 5. Schematic of sampling system in the pilot artificial turf setup constructed by company TURF B.

3.6. Field Studies

3.6.1. Background sampling of soil water

Soil water was sampled at two locations (~3 meters apart) on an irrigated lawn located on Stanford campus using two SW-074 lysimeters (Soil Measurement Systems, Tucson, AZ, Figure 6). Soil water was withdrawn at approximate depths of 5 to 15 cm below ground surface.

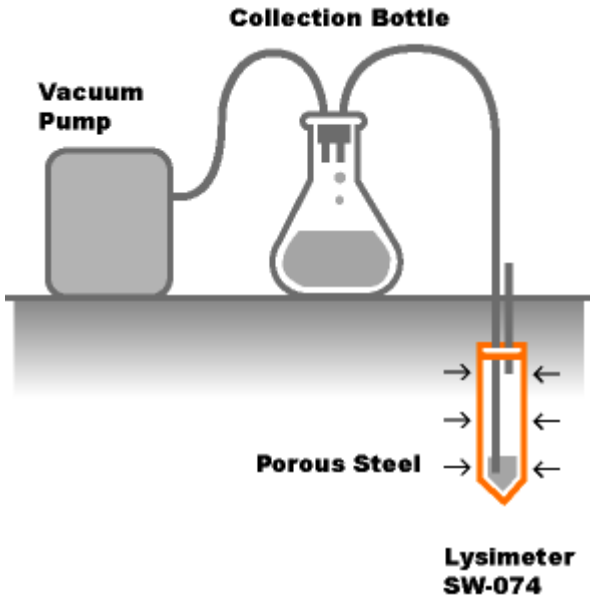


Figure 6. Operation of SW-074 small single chamber suction lysimeter.

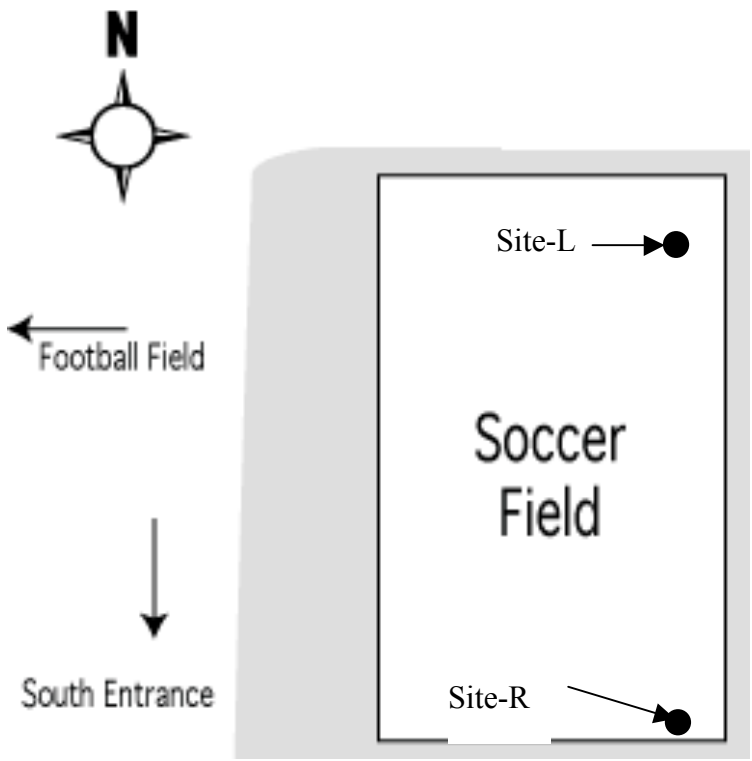
(From http://www.soilmeasurement.com/sw-074.html).

3.6.2. Sampling at the field site

Leachate collection pans were installed at two locations on the field site on 01/23/08. The sites were denoted as Site-L and Site-R, shown in Figure 7. At each site, pans were installed at two depths: (1) immediately below the artificial turf layer and (2)

above the native soil layer. Leachate that accumulated in the collection pans was sampled by suction using a battery-operated vacuum pump. The bottom level collection pans never collected water, however, suggesting that the drainage system worked as designed, efficiently diverting water to the main drainage pipe (which is connected to a storm water drain) and preventing seepage into the subsurface.

(a)



(b)

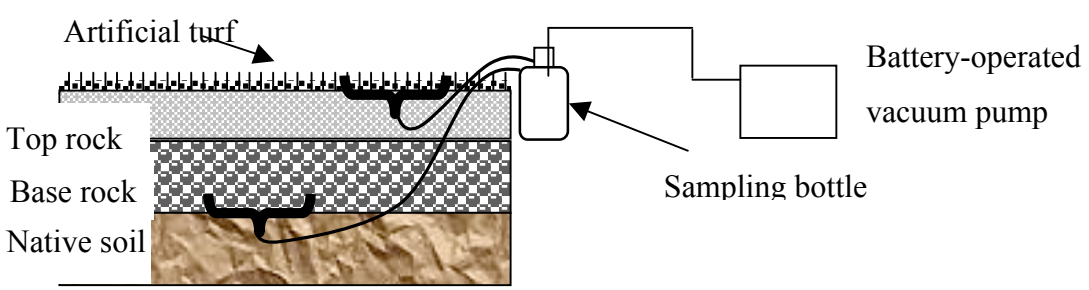


Figure 7. Field site at a local college athletic field: a) schematic drawing of the sampling locations in the soccer field; b) installation of the sampling system at the top and bottom layer.

4. RESULTS

4.1. Chemical Characterization of Artificial Turf Components

4.1.1. Particulate heavy metals in fresh crumb rubber

Figures 10a-c show SEM pictures of surfaces of fresh crumb rubber from artificial turf and results of EMPA analyses of the highlighted particles. Spectra indicate the presence of zinc, iron, and titanium, consistent with the presence of oxide (ZnO), elemental iron (Fe), and titanium oxide (TiO_2) particles. ZnO and TiO_2 particles are components of tire rubber. The ZnO particles were approximately 1 μm in size and occurred embedded in the rubber and at the particle surface. The iron particles were 10 μm to 20 μm in diameter and were detected only at the particulate surfaces. The Fe particles probably originated from shredded steel components.

The TiO_2 particles were smaller (<0.5 μm) and less abundant than ZnO particles. TiO_2 is commonly used as a white pigment in tire manufacturing. ZnO, Fe and TiO_2 particles are leachable and obvious sources of Zn, Fe, and Ti. Specific source materials for other metals (in particular for lead), if present, were below the detection capability of the EMPA instrument used.

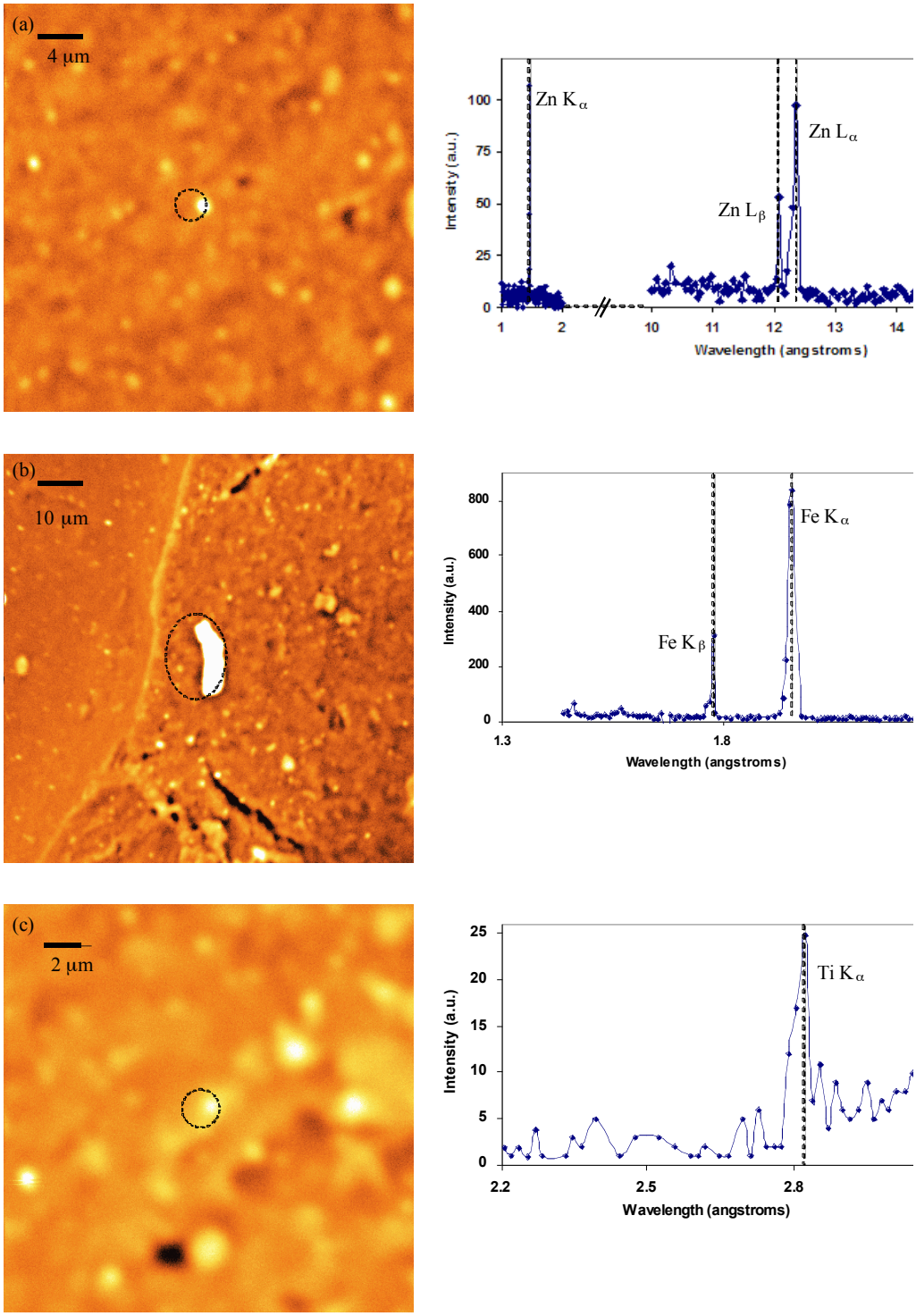


Figure 10. SEM and EMPA results of particles in rubber tires: ZnO (a); iron (b); and TiO_2 (c) particles.

4.1.2. Metal contents in fresh rubber crumbs used as infill

Figure 11 compares the total heavy metal contents in crumb rubber samples of fresh TURF A and TURF B (determined after ashing, as described in Section 3.3.3.). The profiles of the heavy metals contained in the TURF A and TURF B samples were very similar with Zn being most abundant. The relatively high content of Zn (approximately 20 mg/g), Fe (0.2-1.6 mg/g), and Ti (0.11-0.26 mg/g) is consistent with manufacturing data and the detection of these metals by EMPA. Co, Fe, Mo, Pb, Sn, and Ti were present at levels averaging approximately 0.01 mg/g to 1 mg/g, whereas Ba, Cr, Mn, Ni and Sr concentrations were below 0.01 mg/g.

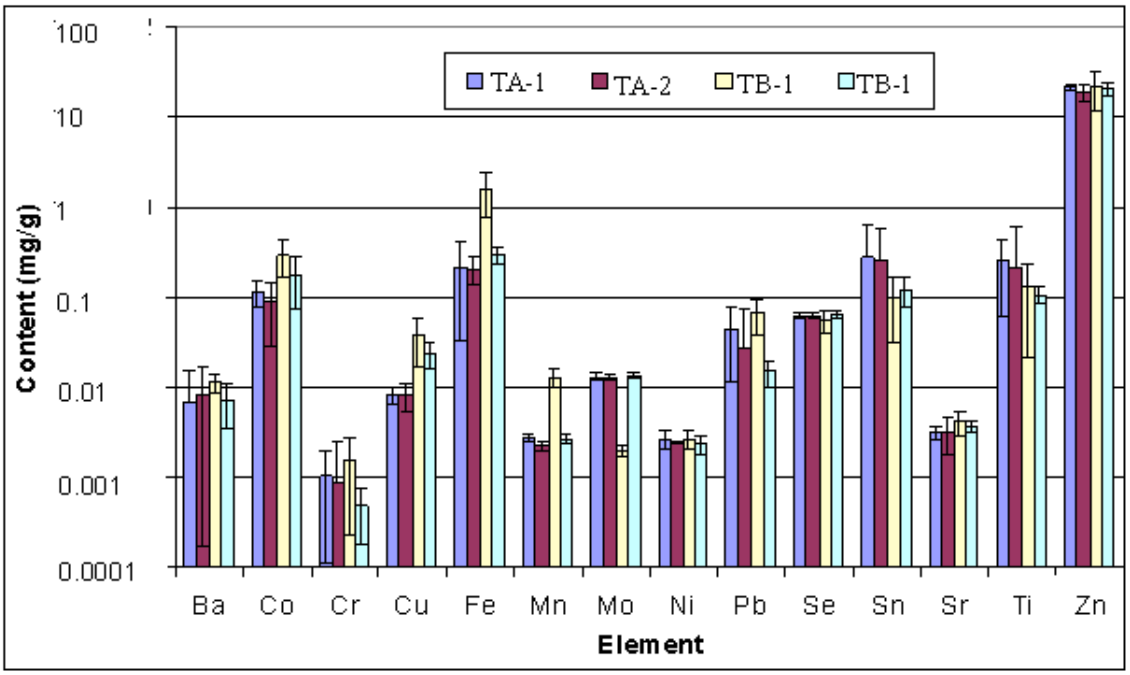


Figure 11. Heavy metal contents in crumb rubber samples of TURF A (TA-1 and TA-2) and TURF B (TB-1 and TB-2).

Values and error estimations were obtained from three measurements of three subsamples. Error bars represent 99% confidence intervals (CI) of measurements of triplicate sub-samples.

4.1.3. Metal contents of rubber crumbs from four sports fields

Samples of rubber crumb from four local sports fields, GI, GR, MH, and OG, were analyzed for metals to determine representative heavy metal contents. At the time of sampling, the MH site was still under construction and materials were fresh, i.e., unweathered. Results are indicated in Figure 12. The metal profiles of the four materials were remarkably similar. Zn was most abundant with contents ranging from approximately 13.8 mg/g to 20.8 mg/g. Co, Fe, Mo, Sn, and Ti were present at levels within the 0.01 mg/g to 1 mg/g range and Ba, Cr, Fe, Mn, Ni, Pb and Sr were below 0.01 mg/g. Zn content in the fresh rubber from MH site was comparable to those in TURF A and TURF B (~20 mg/g), while those in the older fields were lower, suggesting gradual loss of Zn from crumb rubber over time.

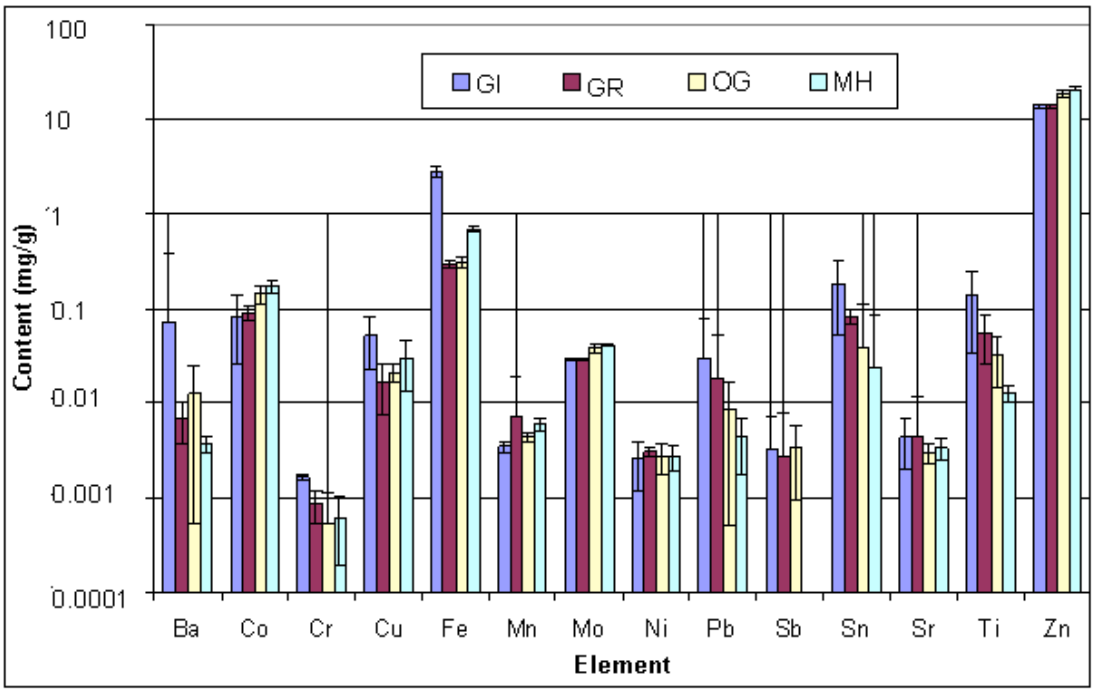


Figure 12. Total heavy metal contents in crumb rubber samples from the artificial turf fields of GI, GR, OG, and MH.

Error bars represent 99% CI of measurements of triplicate samples.

4.1.4. Metal contents of fiber blades, carpet backing, and geotextiles

Figure 13 shows the heavy metal contents in fiber blade and carpet backing materials of TURF A and TURF B. Values reported in Figure 13 are mean values of duplicated measurements of samples.

Figure 13a shows that Al (1.2-2.1 mg/g) and Fe (2.7-4.0 mg/g) were the most abundant in the fiber blade samples (>1 mg/g). The averages of Cr, Cu, Mg, Mn, Ni, Sn, and Ti were in the 0.01 mg/g to 1 mg/g range, and Ba, Co, Mo, Pb, and Sr were below 0.01 mg/g. These data indicated that fiber blade materials were unlikely sources of Zn or Ti. Fiber blades, which typically consist of polyethylene, may also contain additives such as coloring pigments and UV inhibitors (for photoresistance). The trace levels of heavy metal that were detected may have stemmed from some of these additives. Lead (close or below 0.001 mg/g) may have been an impurity; lead is not commonly a component of additives.

Figure 13b summarizes the heavy metal contents measured in samples of carpet backing materials of TURF A and TURF B. The dark-gray carpet backing is a composite of polypropylene, polyamide 6, polyolefins, and/or polyurethane. The plastic matrix of carpet backing contained particulates, probably consisting of inorganic matter. No carpet backing could be obtained for TURF B-2. Filter paper was used as a blank control sample. Ca (7-8%), Mg (0.3-1.3%) and Fe (0.9-2.0 mg/g) were typically present above 1 mg/L and may have been associated with the particulates. Strontium (Sr), which was present within the range of 0.16-0.32 mg/g, co-occurs naturally with calcium in calcite and dolomite. Zn, often a component of additives, was present at trace levels (0.01-0.04 mg/g). Ti was detected in all cases except in one TURF B sample.

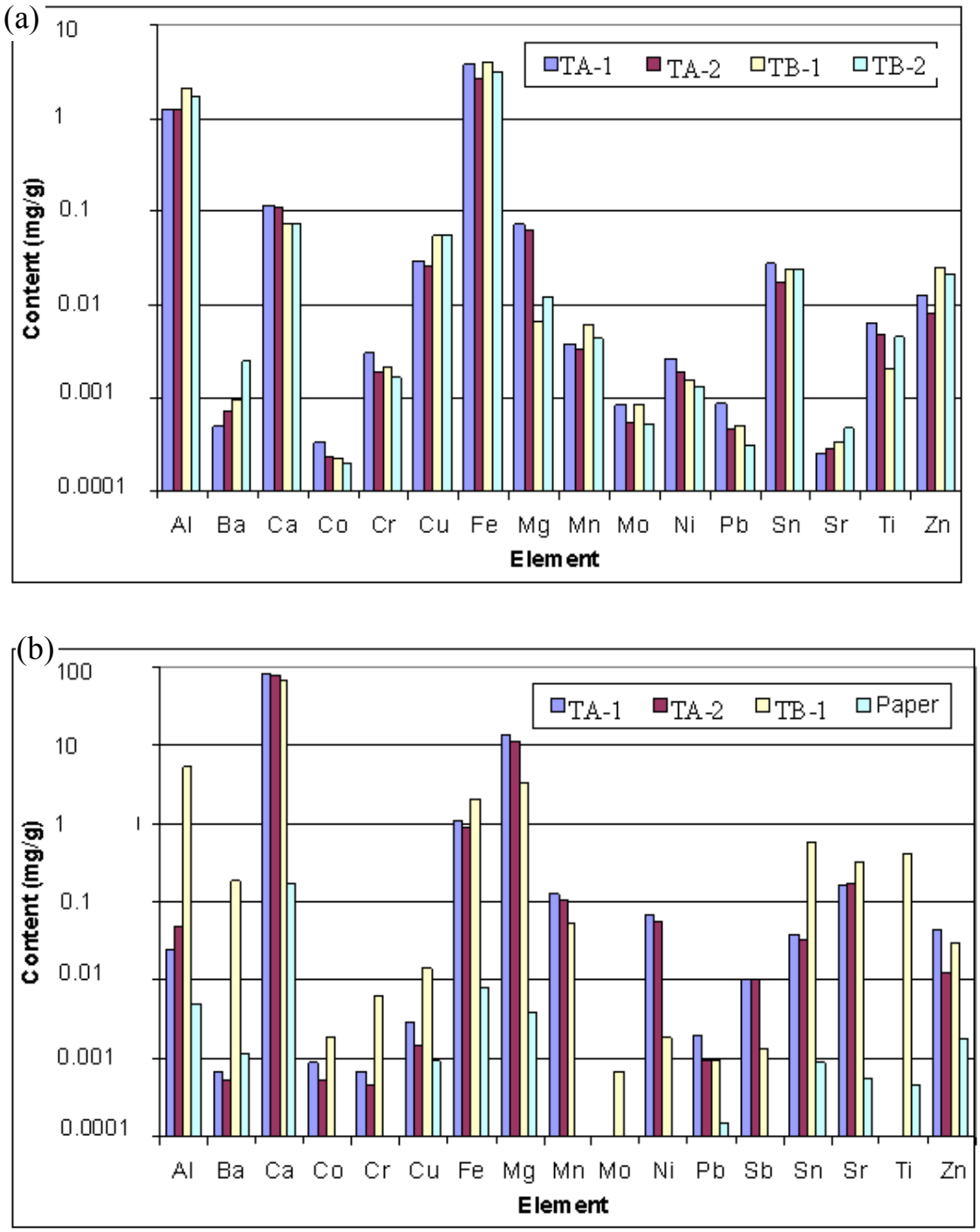


Figure 13. Metal contents in (a) fiber blade and (b) carpet backing samples of TURF A and TURF B.

Filter paper was used as a blank control.

Figure 14 depicts the heavy metal contents in the fiber blade, carpet backing material, and geotextile used in the artificial turf field (TURF C) at site MH. Although geotextile is typically used in all artificial turf fields, we could only obtain it from the MH field site, which was under construction during this investigation. It appears that the metal contents in TURF C differ significantly from those observed in TURF A or TURF B. In the fiber blade material, the contents of Fe (14.3 mg/g) and Zn (7.6 mg/g), Ti, Sn, Cu and Ni were higher than those for TURF B and TURF A. The carpet backing showed relatively high contents of Fe (2.7 mg/g), with some Mn (0.3 mg/g), Ni (0.15 mg/g), Sn (0.32 mg/g), Sr (0.15 mg/g) and Zn (0.02 mg/g). In contrast, the metal contents in the geotextile material were much lower. The only metals present at relatively high levels were iron and lead (>0.1 mg/g). These results are in agreement with conclusions made for TURF B and TURF A, indicating that carpet and geotextile materials are unlikely major sources of heavy metals in leachate. The fact that fiber blades of TURF C contains relatively high metal contents compared to TURF A and TURF B (likely stemming from added pigments and UV inhibitors) indicates the need to test fiber blade materials on a case by case basis.

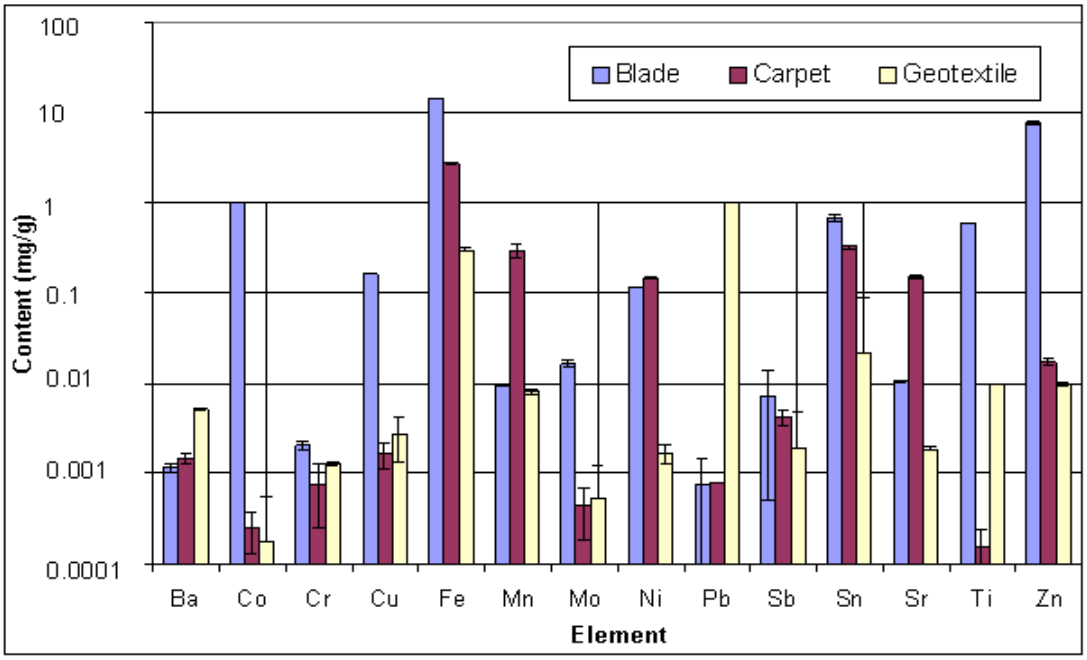


Figure 14. Total heavy metal contents in the fiber blade, carpet backing material, and geotextile used in the artificial turf field at site MH (TURF C).

Error bars represent 99% CI of measurements of triplicate samples.

4.2. Leaching of Zinc under Laboratory Conditions

4.2.1. Batch experiments: leaching of infill, fiber, and carpet backing by Milli-Q water

Figure 15 shows the distribution of metal species found in the leachate of rubber crumb from four pieces of artificial turf in sequential batch leaching experiment by Milli-Q water in one round of the sampling. Only Al, Ca, Na, and Zn were found at significant levels in the leachate. Al, Ca, Na were also found at comparable levels in our control samples and their presence was caused by leaching from the glassware used in this study. Of the heavy metals, zinc is the one that appears to be of the greatest concern in the leachate of rubber crumb. This conclusion is consistent with the distribution of heavy

metals in the rubber crumb of artificial turf. Because zinc was the only heavy metal species found at significant levels, only Zn data is discussed in the rest part of this section.

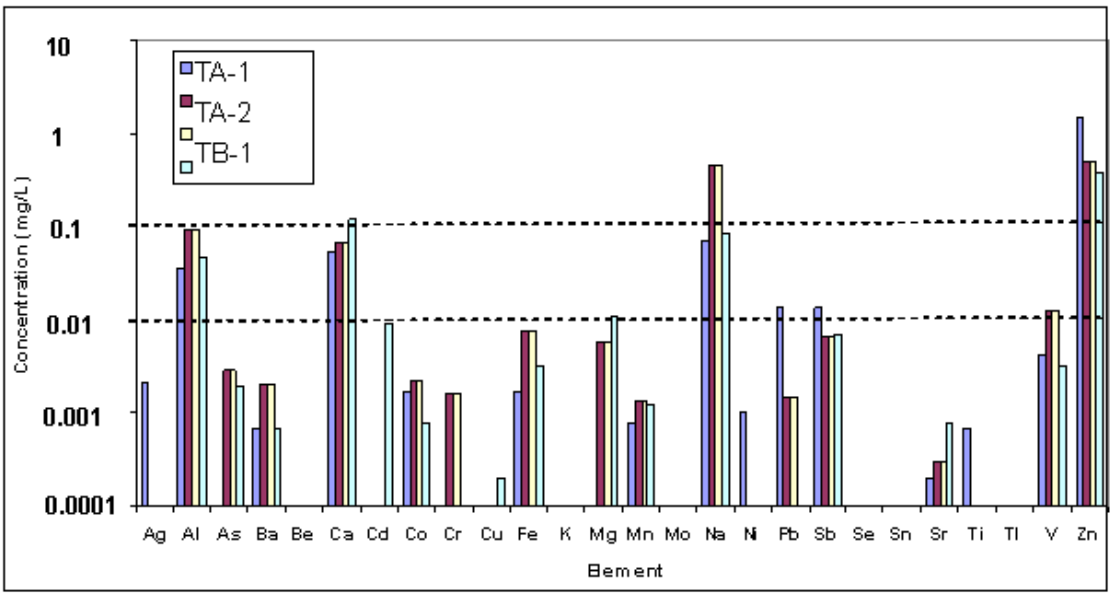


Figure 15. Distribution of metal species found in the leachate of rubber crumb from artificial turf in sequential batch leaching experiment by Milli-Q water (results from the 12th sampling event).

Leaching of Zn from infill, fiber, and carpet by Milli-Q water was examined in series of controlled laboratory studies (two samples each of TURF A and TURF B). Figures 16a - d shows the amounts of zinc that leached over a period of approximately 10,000 hours (416 days). The data demonstrate infill was the principal source of Zn; leaching from fibers and carpet backing was insignificant. Zn leaching was fast initially and then slowed, but continued even after one year of exposure. The TURF A samples (#1 and #2) leached approximately 1 mg/g after 416 days; in the case of TURF B samples, the final amount was approximately 0.3 mg. For TURF A, 1 mg/g corresponds to approximately 5% of the initial Zn content (20 mg/g). Compared to TURF A, TURF B infill leaches because rubber crumbs are 50% diluted with sand. TURF B data was more

variable than TURF A data because of the variable crumb rubber to sand ratios obtained in the sub-samples. None of the fiber blade and carpet backing materials release zinc, except for trace quantities.

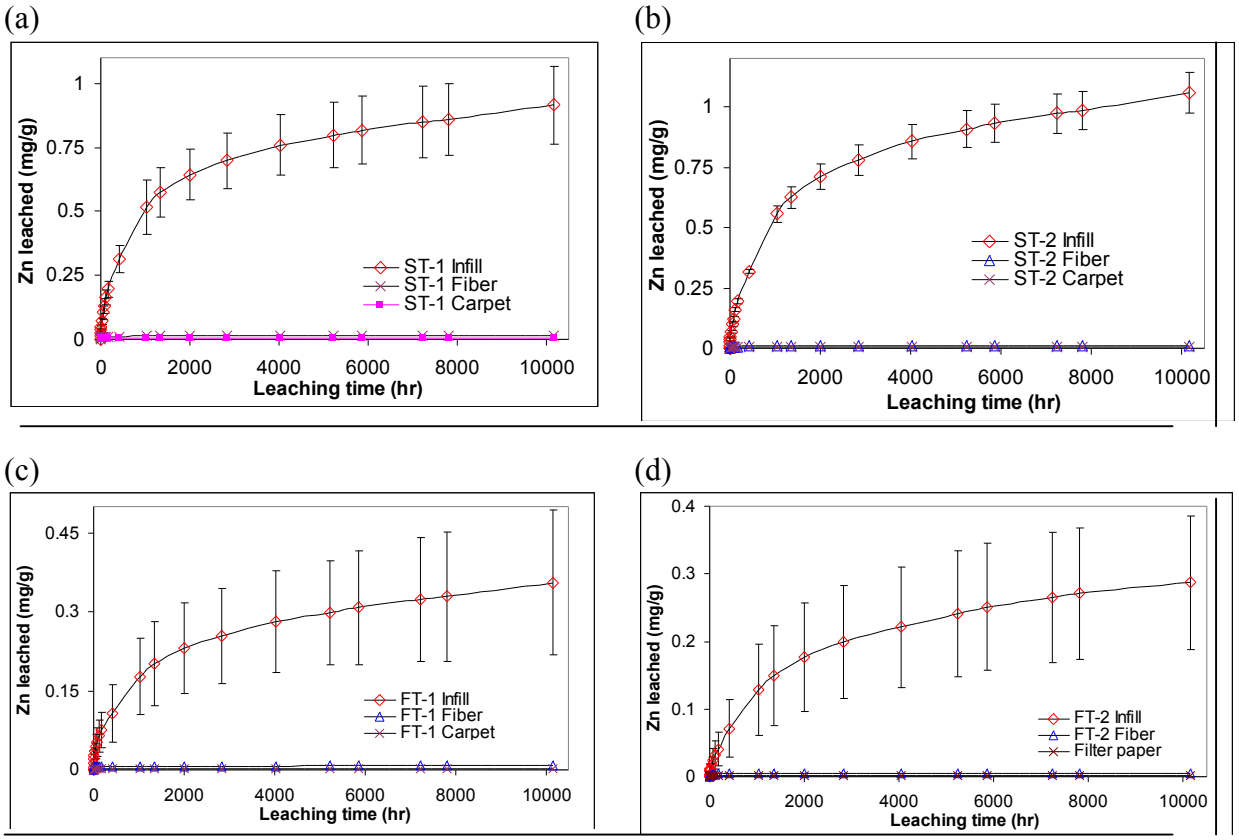


Figure 16. Cumulative leaching of zinc from artificial turf components in Milli-Q water: (a) TURF A sample #1 (TA-1); (b) TURF A sample #2 (TA-2); (c) TURF B sample #1 (TB-1); and (d) TURF B sample #2 (TB-2).

Error bars represent 99% CI of measurements of triplicate samples (i.e., 3 samples were prepared and analyzed 3 times each upon sampling).

4.2.2. Batch experiments: leaching of crumb rubber by synthetic rainwater and acidic rainwater

To examine leaching of Zn under more realistic conditions, samples of TURF A and TURF B crumb rubber were leached by synthetic rainwater for 6,400 hours (or 267 days). To facilitate comparison of the two materials, leaching studies here were done with the rubber components only, i.e., excluding sand in the TURF B samples. Samples from existing artificial turf fields, GI, GR, and OG, were also evaluated using the same test. Figures 17a and b show that leaching was first rapid and decreased with time, similar to that observed with Milli-Q water.

Synthetic rainwater leached 0.76 and 0.57 mg/g of Zn, or 3.8% and 2.8%, respectively, from the TURF A and TURF B samples (Figure 17a). Zn leaching rates from the TURF A rubber in the synthetic rainwater (pH=5.5-5.6) were close to those observed in Milli-Q water (Figure 16). This observation suggests that the composition of rainwater (mainly Cl^- and SO_4^2) commonly present in rainwater (section 2.1) did not influence Zn leaching.

The TURF A crumb rubber released Zn more rapidly than TURF B crumb rubber (after separation from sand). The appearance of the rubber particles suggested that crumb rubber TURF B was produced by cryogenic processing; by contrast, it appeared that TURF A crumb rubber was probably produced by grinding.

On average, the OG samples leached 0.97 mg/g, significantly more than the GI and GR samples, which leached 0.45 mg/g and 0.33 mg/g, respectively (Figure 17b). Its higher specific surface area may have caused the observed rapid leaching. Visual inspection indicated that it contained a relatively large fraction of small particles.

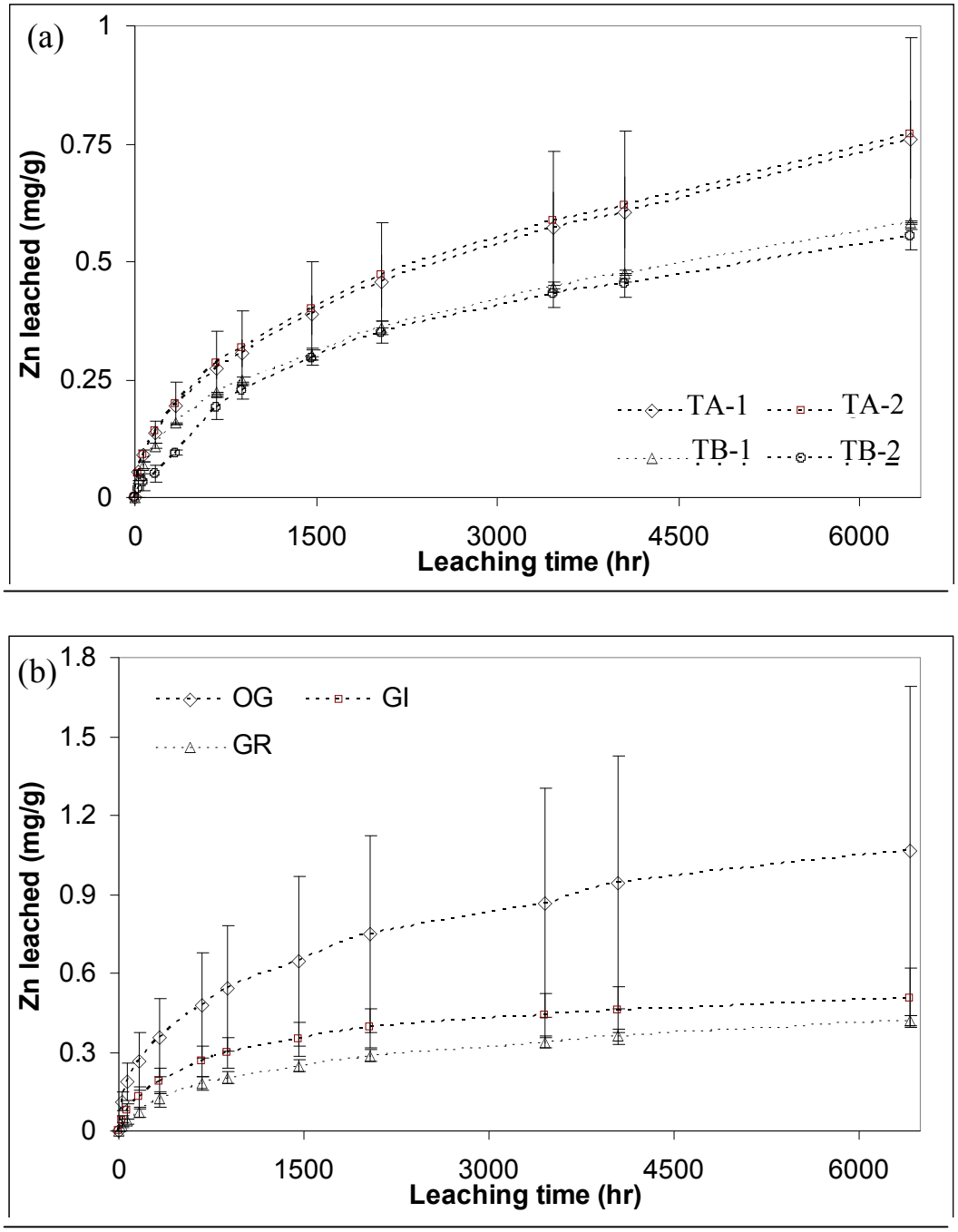


Figure 17. Leaching of zinc from artificial turf components in synthetic rainwater: (a) two TURF A (TA-1 and TA-2) and TURF B samples (TB-1 and TB-2) provided by the manufacturers; and (b) three samples from existing fields: GI, GR, and OG.

Error bars represent 99% CIs of 3 samples.

Figures 18a and b show the amounts of Zn leached by synthetic acid rainwater (pH 3.4-3.5) from the various crumb rubber samples. In all cases, leaching was fast initially and slowed with time. During 4,700 hours (196 days), the crumb rubber samples leached 0.93 and 1.03 mg/g Zn (from TURF A), and 0.68 and 0.69 mg/g Zn (from TURF B), corresponding to 4.8% and 3.4%, respectively, of the total Zn present (~20 mg/g). As in synthetic rainwater, Zn leached at a slower rate from TURF B than from TURF A. Among field samples the OG samples leached at a significantly faster rate than the GI and GR samples (Figure 18b). In the synthetic acid rainwater, the leaching rates of Zn from the three field rubbers were approximately two times higher than those in the (non-acidified) synthetic rainwater.

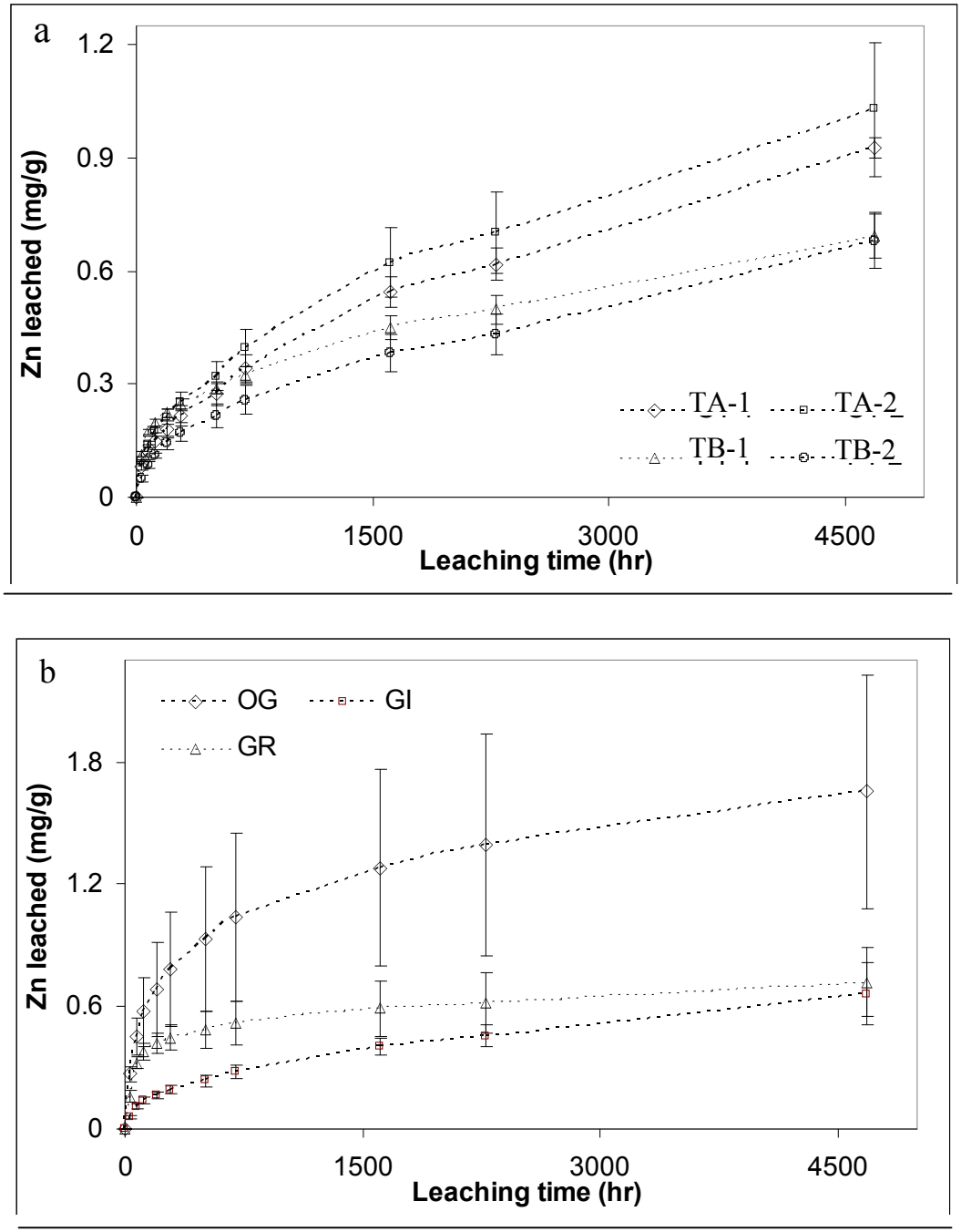


Figure 18. Quantity of Zn cumulatively leached from artificial turf components by synthetic acid rainwater: (a) two TURF A (TA-1 and TA-2) and TURF B samples (TB-1 and TB-2) provided by the manufacturers; (b) samples from GI, GR, and OG.

Error bars represent 99% CIs obtained by analysis of 3 samples.

Table 2 summarizes final Zn leaching data (4,500 h). Low pH promotes Zn leaching. This effect is attributed to more rapid dissolution of ZnO particles or perhaps faster degradation of the rubber matrix in the acidic medium. In both synthetic rainwater and synthetic acid rainwater, Zn release was faster from TURF A rubber than from TURF B rubber.

Table 2. Zn leached by Milli-Q, synthetic rainwater, and acid rainwater from different infill materials (mg/g) after 188 days (4,500 h) of leaching.

Source	Milli-Q water	Synthetic rainwater pH 5.5-5.6	Synthetic acid rainwater pH 3.4-3.5
TURF A-1	0.78	0.63	0.9
TURF A-2	0.89	0.64	0.98
TURF B-1	0.29*	0.49	0.66
TURF B-2	0.23*	0.47	0.65
OG	no data	0.98	1.61
GI	no data	0.48	0.62
GR	no data	0.39	0.68

*--The infill materials were a mixture of silica sand and crumb rubber (other samples were crumb rubber only).

4.2.3. The influence of sunlight exposure and temperature on leaching rates evaluated using column tests

Crumb rubber samples from the artificial turf at a local high school athletic field (GR) were used to evaluate the impact of sunlight and heat on leaching. Following exposure to sunlight and heat, samples were tested using synthetic rainwater and the column tests described in Section 4. Leaching was determined using simulated rain intensities of 2.17 and 4.33 inch/hour. Figure 19 shows the Zn concentration measured in column effluent (leachate) samples (left y-scale) and the cumulative amount of Zn leached from the column (right y-scale). The x-axis shows only the leaching time, i.e., the time water was percolating through the column. Individual leaching experiments lasted 48 to 100 min and were followed by an approximately 22 h rest period during which the column was allowed to drain. During the rest periods, the column retained pore water and remained wet.

The spikes of Zn observed after the resting periods indicates Zn release into the stagnant pore water continues during the resting period. During continuous leaching, concentrations are much lower and continue to decrease. The first leachate sample obtained contained 0.49 mg/L Zn. After the initial sharp drop, concentrations decreased slowly to reach approximately 0.07 mg/L towards the end of each the experiment. This pattern was repeated in the following simulated rain events. Unexpectedly, doubling the rain intensity to 4.33 inch/hour did not proportionally decrease the Zn concentration.

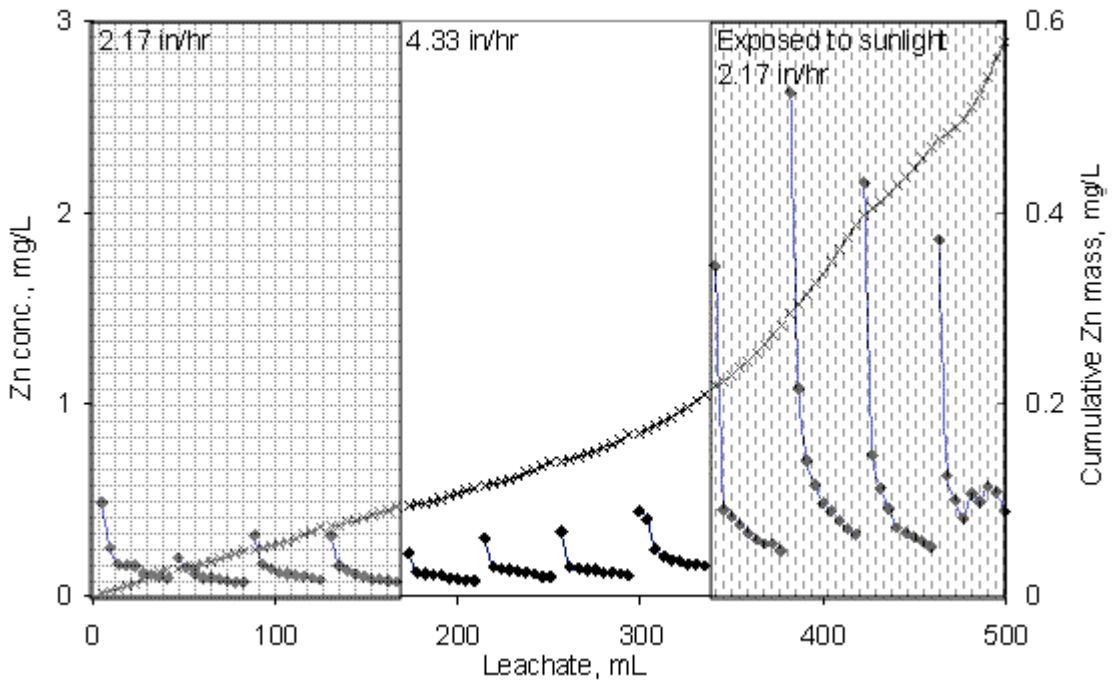


Figure 19. Zn leaching by artificial rain from the crumb rubber packed in a glass column at 2.17 and 4.33 inch/hour and after heating to 55°C and exposure to sunlight. Shown are leachate concentrations in column effluent samples (mg/L, left y-scale) and cumulative mass of Zn leached (mg/g, right y-scale).

Experimental details are indicated in Section 4.

During exposure to sunlight, the temperature of the rubber particles was kept constant at 55°C. This temperature may be expected to occur at the surface of an artificial turf field during on a sunny summer day in the Bay Area. After exposure, rubber particles were cooled to room temperature (23°C) and re-packed into the column.

After sunlight exposure, the initial leachate Zn concentrations were in the range of 1.7 to 2.6 mg/L, 4 to 5 times higher than without sunlight exposure. At the end of the simulated raining events, the Zn concentrations decreased to 0.2 to 0.4 mg/L, more than twice as high as without sunlight exposure. These results indicate that conditions of a hot sunny day, i.e., heat and sunlight irradiation, promote leaching of Zn from the crumb

rubber. A possible explanation is that the combined effects of light and heat degrade or crack of the surface of crumb rubber thereby exposing ZnO particles to leachate.

A series of similar experiment were conducted to isolate the effects of heat and sunlight on Zn release. Results are depicted in Figure 20 following the format of Figure 19. Experimental conditions were as described in Section 2.4.2 and in the experiments described above, with the following exceptions. Crumb rubber particles were either heated to 55°C for 20 h or irradiated by the photosimulator for 20 h or 66 h. During sunlight exposure, the temperature was controlled at 22°C using a water bath.

Figure 20 shows in sequence ambient conditions, 55°C heating without sunlight, and sunlight irradiation without heating. The effect of heating is indicated by comparing leaching under ambient conditions (first 160 h) with the leaching at 55°C (160 h to 320 h). Data indicate that heating promotes the release of Zn. Possible causes are heat-induced degradation of the rubber matrix, faster diffusion of metal ions to the rubber surface at higher temperature and more rapid dissolution of Zn oxide. Comparing heating data (160 h to 320 h) with irradiation data (320 to 500 h) indicates that sunlight exposure promotes Zn release even in the absence of heating. Increasing the irradiation time increases the amount of Zn that becomes leachable. After extending exposure from 22 h to 66 h, the Zn concentrations in the initial leachate samples increased several fold.

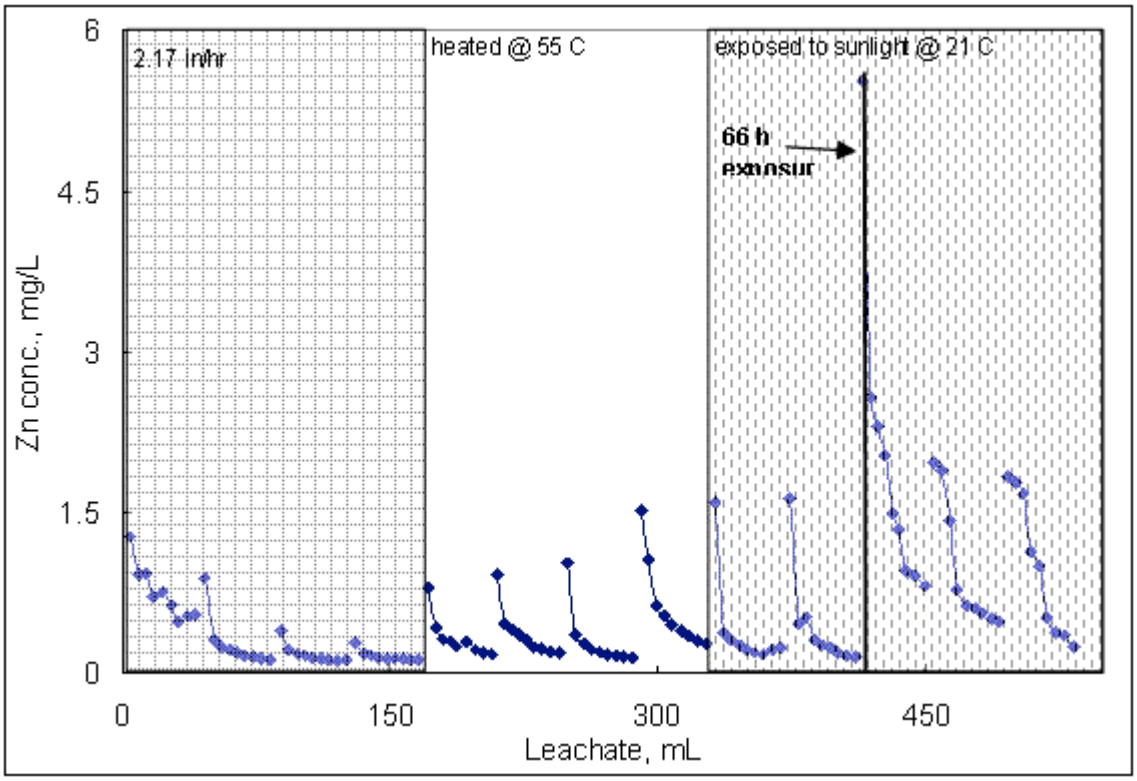


Figure 20. Zn leaching from the crumb rubber packed in a glass column using the crumb rubber obtained from GR field site.

4.2.4. Sorption and desorption of heavy metals from rock materials underlying artificial turf

Calcium carbonate is the major component of the crushed rock materials underlying the artificial turf. Literature data indicates that rocks could play an important role in immobilizing the heavy metals released from artificial turf. A series of laboratory batch and column tests were conducted to study whether crushed rock materials used to support artificial turf fields attenuate metals that may be present in leachate. Table 3 summarizes the calcium carbonate contents measured in the top and bottom rock materials used in the TURF C and TURF B pilot setups. The top and bottom rock materials in the TURF C pilot contained the same amount of $CaCO_3$ (approxmately 12%), whereas in the TURF B setup, the $CaCO_3$ contents in the top and bottom layers

differed (16% in the top and 5% in the bottom). The top and bottom rock materials in the TURF C pilot setup originated from the same quarry. In contrast, the top rock material supplied with the TURF B pilot setup appeared to be mudstone, while the bottom rock material consisted of river pebbles.

Table 3. Calcium carbonate content in supporting rock materials used in the pilot setups.

$CaCO_3$ content*	Top layer (%)[#]	Bottom layer
TURF C pilot setup	11.6 ± 0.1	11.9 ± 0.4
TURF B pilot setup	16.0 ± 1.2	4.7 ± 0.6

* — Determined based on "loss-on-ignition" method

— Means and standard deviations of triplicate samples.

Figures 21a and b, respectively, depict the breakthrough and leaching behavior of Zn in rock materials. Figure 21a depicts the breakthrough curve of Zn in the effluent of a column packed with the top rock material as used in the TURF C pilot setup and fed with synthetic leachate containing 1.0 mg/L Zn and 0.05 mg/L each of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, and V. In the effluent, only Zn was detected, while the other metals were below the detection limits (0.001-0.005 mg/L). Significant attenuation of Zn was observed. After 36 hours of continuous feeding, the Zn concentration in the column effluent was less than 5% of that in the feed. Based on the sorption breakthrough curve, the total mass of Zn sorbed on the rock materials was 0.013 mg/g during the experiment. Overall, these results indicate that the top rock materials effectively retained Zn. Assuming that 14.4 inches of annual rainfall leach artificial turf and produce leachate with 1 mg/L Zn (which is representative for concentrations observed in field samples), it may be estimated that a 4-inch layer (top layer alone) of TURF C rock materials attenuates leachate to below 0.05 mg/l for approximately 5 years. This estimate should be verified by longer-term experiments and considering a wider range of conditions and materials.

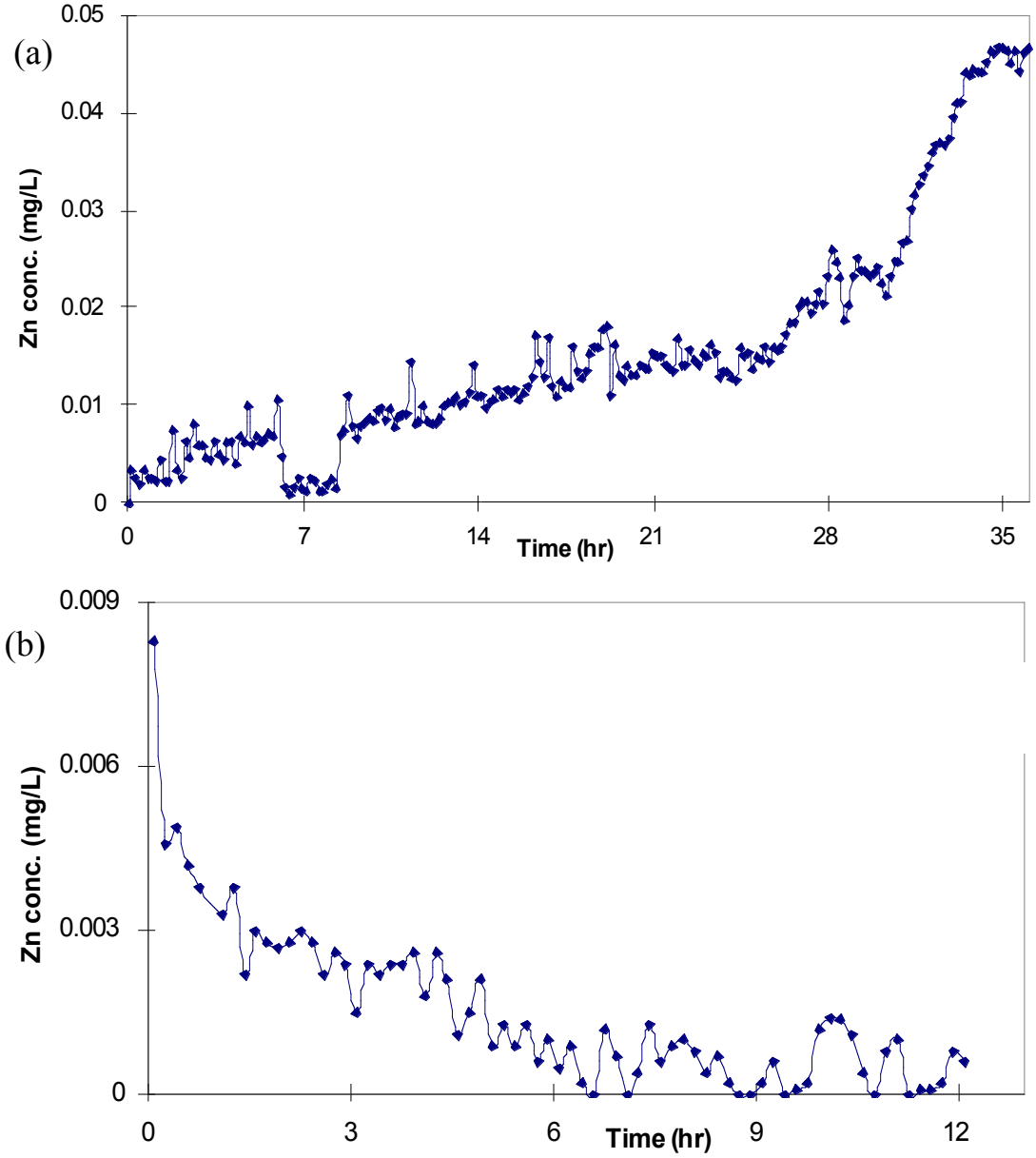


Figure 21. Sorption (breakthrough) (a) and desorption (leaching) (b) of Zn from the same top rock material used in TURF C pilot system

(For conditions see text; influent Zn concentration is 1.0 mg/L Zn.)

Desorption was studied to evaluate the potential for remobilization of metals by synthetic rainwater. Figure 21b shows the Zn desorption (leaching) curve of the top rock material that was loaded with Zn during the sorption experiment described above. The leaching curve was obtained by passing synthetic rainwater through the column at a flow rate corresponding to 2 in/h rainfall. The effluent Zn concentration was initially approximately 0.009 mg/L but decreased rapidly (within 6 hours) to approximately 0.001 mg/L. The total amount of Zn that was mobilized during 12 hours of leaching was small (<0.07% of retained in the column), which suggests that the rock materials sorbed Zn strongly. However, to generalize the conclusion that Zn is not readily mobilized would require evaluation of a wider range of conditions. A more detailed discussion of the attenuation of Zn by the rock materials is given in section 5.4 Geochemical Modeling.

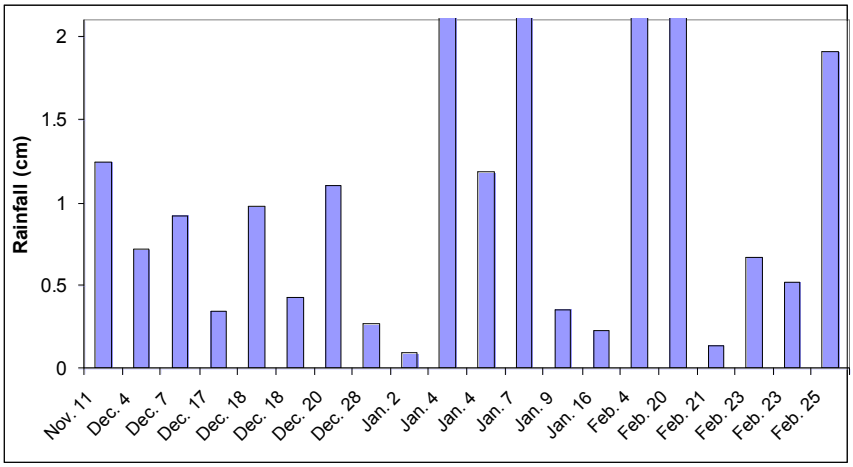
4.3. Pilot Studies

4.3.1. Metal release under natural rainfall conditions

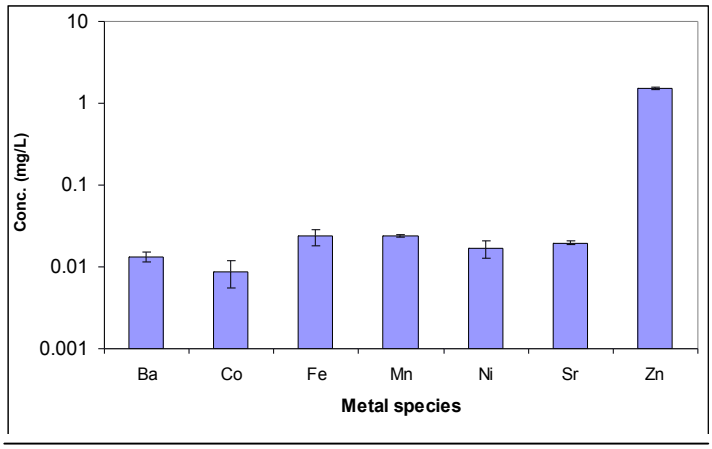
Metal release under natural rainfall conditions was studied using two the pilot setups equipped with sampling devices, as described in Section 3.5. Figure 22a shows rainfall measured at the location of the pilot setups (Stanford campus) during the 2007-2008 rainy season. The rainfall amounts ranged from 0.1 cm in minor rain events to >2.1 cm in heavy rainstorms. Sampling was continuous during the rainy season except Jan. 16 through Feb. 4. Several heavy rain events exceeded the capacity of the samplers and prevented obtaining samples.

A typical example illustrating the distribution of heavy metals in leachate is shown in Figure 22b. The sample was obtained on 12/17/07 in one of the small setups, i.e., in the sampling pan that collected leachate from the artificial turf layer (note log scale of plot). As expected from batch study results, Zn was the most abundant heavy metal species. Concentrations of Ba, Co, Fe, Mn, Ni, and Sr were approximately 0.01 mg/L, two orders of magnitude lower than Zn. The other heavy metals tested were below the detection limits (0.005-0.01 mg/L).

(a)



(b)



(c)

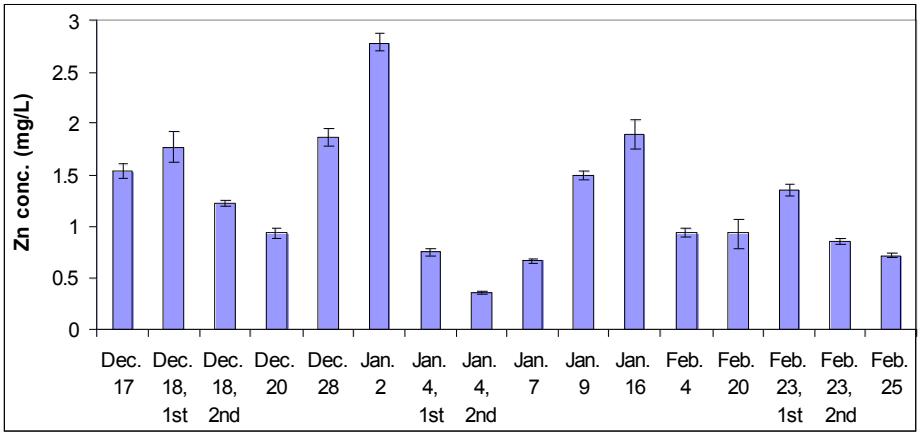


Figure 22. Heavy metal contents in the leachate from small setup: (a) rainfall history; (b) major metals in the leachate collected on 12/17/07; and (c) Zn concentrations after rainstorms. Heavy storms prevented sampling between Jan. 16 and Feb. 4.

Figure 22c shows the concentration of Zn in the leachate of the small setup for different rain events; concentrations ranged from 0.3 to 2.8 mg/L. Comparing the volume of individual rain events and Zn concentrations (Figures 22a and 22c) indicates that short rain events generally produce leachate with higher Zn concentrations. This effect is most evident for samples that were collected on the same day, i.e., Dec. 18, Jan. 4, and Feb. 23. Zn concentrations decreased from the first to the second sample, consistent with high Zn concentrations in first flush samples.

4.3.2. Attenuation of metal in supporting rock beds

Metal concentration was measured in leachate produced by the TURF C and the TURF B pilot setups during the 2007/8 rainy season (Figure 23). Figure 23a compares the concentration of Zn in leachate produced during five rainfall events. Zn concentrations were measured in leachate collected below the artificial turf layer, the fine rock layer, and the coarse rock layer. The artificial turf data represent unattenuated leachate concentrations. Samples denoted as "Fine rock" percolated through the upper (fine) rock layer and samples denoted as "Coarse rock" percolated also through the lower (coarse) rock layer. Zn concentration in the leachate from ground rubber ranged from 0.4 to 1.6 mg/L. Percolating through 4-inch of fine rock attenuated Zn concentrations to 0.006 to 0.02 mg/L; in combination, the fine and the coarse rock layers attenuated Zn to 0.006 mg/L or below. Strong Zn attenuation by rock materials was expected from laboratory column studies and literature reports (Sibrell et al., 2007; Zachara, et al., 1989; Carroll et al., 1998; Zachara et al., 1988 & 1989; Elzinga and Reeder, 2002; Cheng et al., 1998; Temmam et al., 2000).

The Zn concentration in the leachate discharged from the pilot setup remained relatively constant throughout the entire rainy season of 2007-2008, suggesting that it takes more than one season, and probably many more, to exhaust the metal retention capacity of the rock materials. Further work is required to estimate the metal retention capacity of rock beds.

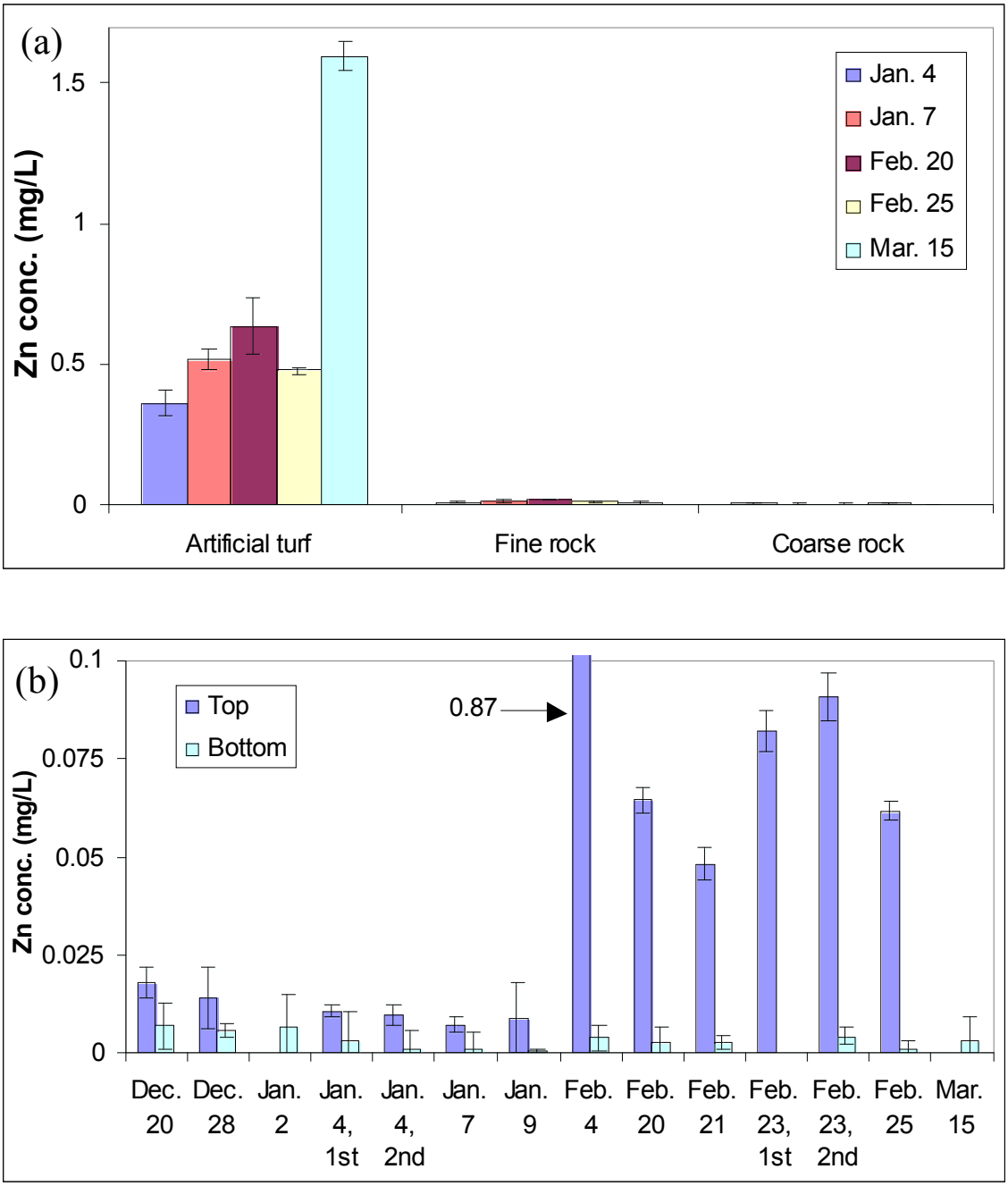


Figure 23. Attenuation of Zn concentration after interacting with rock materials below artificial turf layer: (a) leachate from the TURF C pilot setup, (b) leachate from the TURF B pilot setup.

The TURF B data depicted in Figure 23b compares the Zn concentrations in leachate collected below the artificial turf layer and at the bottom, i.e., before and after

percolation through the TURF B rock bed. In leachate produced by the artificial turf layer, Zn concentrations varied from 0.01 to 0.1 mg/L (due to varying rain intensities). In the leachate discharged from the bottom, i.e., after percolation through the rock bed, concentrations were always less than 0.007 mg/L, indicating significant attenuation. The Zn concentrations in the TURF B leachate were much lower than in the TURF C leachate, presumably because the infill material used in the TURF B setup was diluted with 50% silica sand. Silica sand may also have adsorbed some Zn from the leachate.

The Feb. 4 leachate sample was obtained after a flooding event when heavy rainstorms nearly filled the tank and infill was soaked with rainwater for over three days. Soaking for three days resulted in relatively high Zn concentration at the top. In spite of these elevated concentrations, the leachate concentration at the bottom was only approximately 0.004 mg/L, suggesting that the rock materials maintained sufficient sorption capacity to attenuate Zn.

After the flooding in early February, Zn concentrations in leachate from the artificial turf layer (Top) stayed high for unknown reasons. Perhaps soaking of the artificial turf exhausted the sorption capacity of the sand that may have been effective before the flood or prolonged soaking swelled crumb rubber and made it more leachable. Although the Zn concentrations in the leachate percolating into the rock bed were high, concentrations at the bottom remained low, and there was no evidence for a breakthrough. Concentrations in the discharge continued to be low for the remainder of the study.

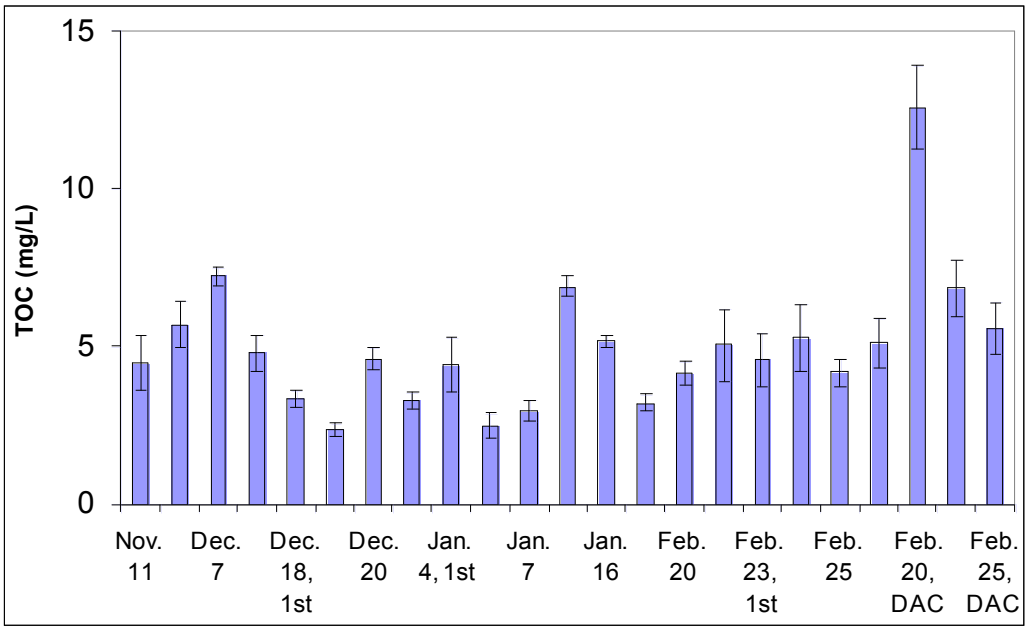
The pilot data suggest that rock beds supporting artificial turf fields can retain a significant quantity of Zn for several years. The time span of this study was too short, however, to extrapolate results to the life span of typical artificial turf fields, which is on the order of 10 to 15 years.

4.3.3. Total organic carbon leaching from pilot systems

Figure 24 shows TOC levels in rainwater and in the leachate from the pilot systems. The TOC levels in the rainwater samples ranged from 3 to 12 mg/L. The high TOC levels in the rainwater probably resulted from accumulation of organic matter (e.g., dust, organic compounds or pollens) on the rainwater sampler, which was washed into the sample bottles by the rainwater. TOC contents in the artificial turf leachate from the small setups ranged from <10 mg/L to 400 mg/L. TOC may have originated from several sources: leaching of organic compounds from the crumb rubber, organic materials deposited from the air onto the artificial turf surface, and rainwater contamination. Tire rubber consists of a complex mixture of natural and synthetic organic compounds in addition to numerous reactive agents and carbon black and other particles. Some of these products can break down be leached out by rainwater.

TOC is an aggregate parameter for organic contamination and generally not a predictor for environmental impacts. The maximum allowable TOC concentration in treated drinking water is 2 mg/L (U.S. Environmental Protection Agency, 1998). Leachate TOC concentrations in the experiments conducted here are comparable to those in runoff from parking lots and highways. Runoff from asphalt parking lot surfaces in metropolitan Phoenix, Arizona was shown to have TOC levels in the range of 26.1 to 295.7 mg/L (Hope et al., 2004). Storm water runoff from six storm sewer outfalls in residential and highway settings in Monmouth County, NJ was found to contain 4 to >100 mg/L organic carbon, which was dissolved (40-90%) or in colloidal (0.01-0.45 µm) form (Tuccillo, 2002). Storm water from urban highway sewer heads in Columbus, Ohio was found to have TOC concentrations ranging from 174 mg/L at the onset of a runoff event to 25 mg/L at the end of the same hydrograph (Gardner and Carey, 2003).

a



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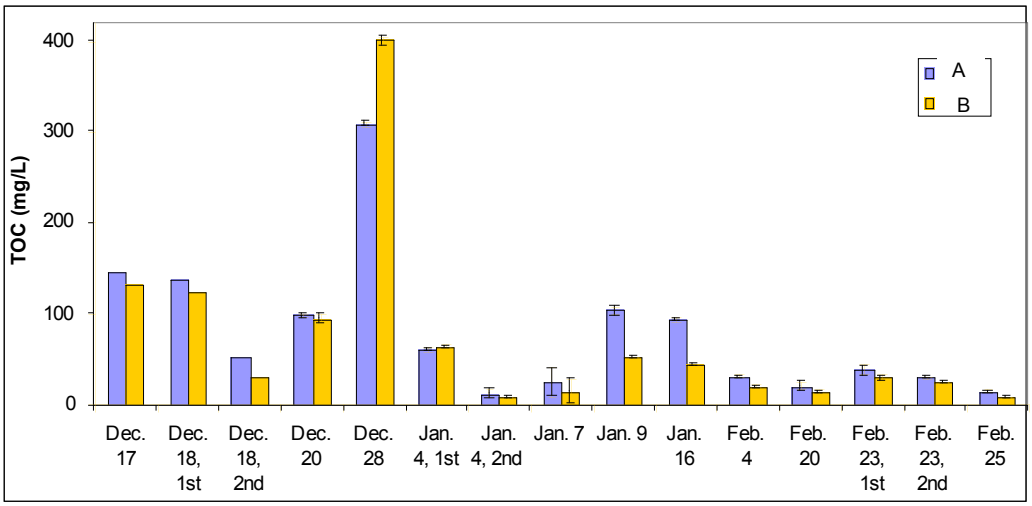

Figure 24. TOC levels in (a) rainwater, and (b) in the leachate from the two small setups (A and B).

Figure 25a compares the TOC contents in leachate of the TURF C pilot setup collected below the artificial turf, the fine rock, and the coarse rock layer. The data indicates that TOC leaching from ground rubber was not significantly attenuated during passage through the fine rock and coarse rock layers.

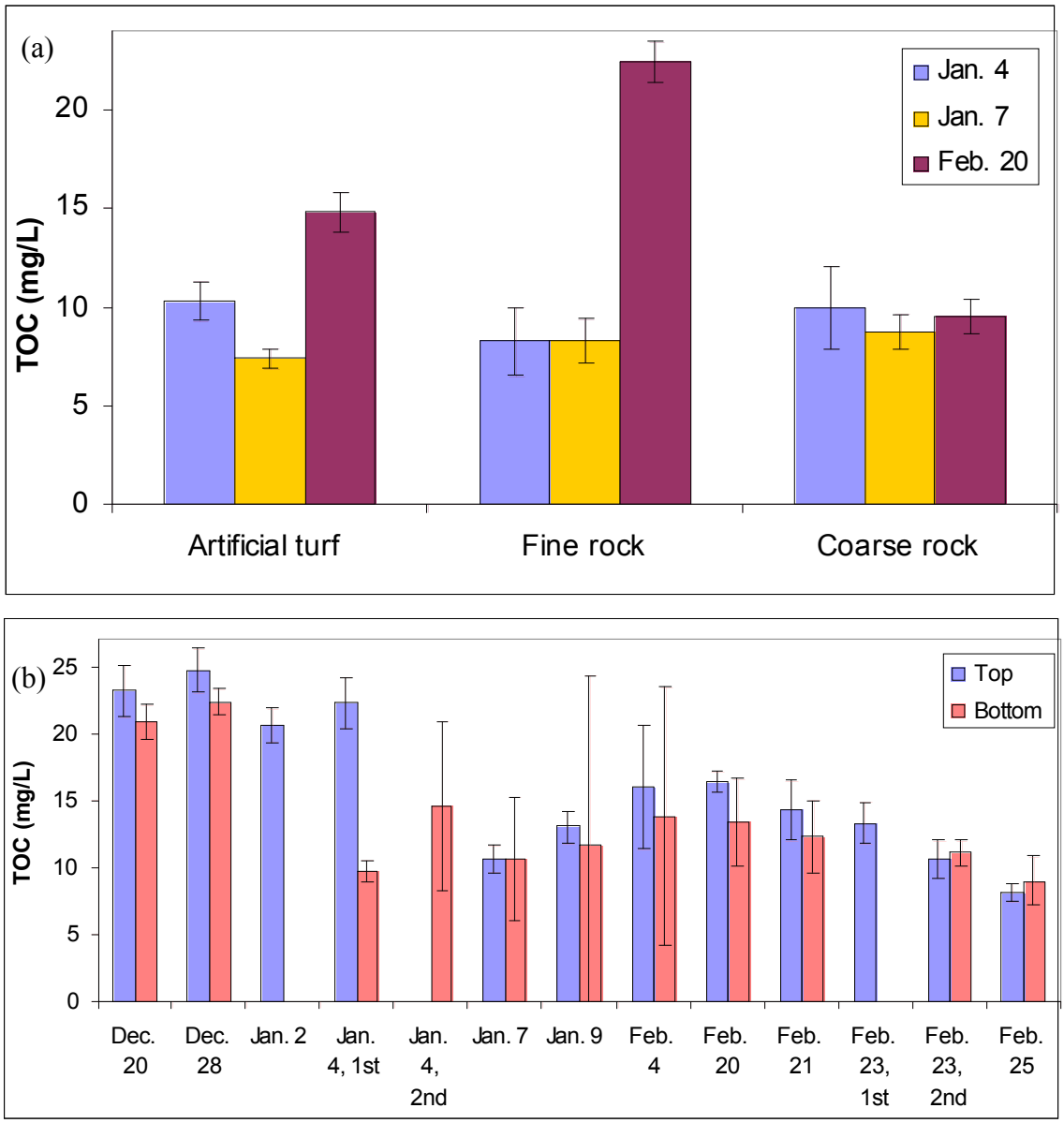

Figure 25. Leachate TOC concentrations produced by the artificial turf at different depths: (a) TURF C pilot setup, (b) TURF B pilot setup.

Figure 25 b depicts the corresponding data for TURF B pilot setup. In this case, the TURF B leachate (top) and percolate collected at the outlet (bottom) were analyzed. Again the data indicate little TOC removal during percolation through the rock materials.

4.3.4. PAH contents in leachate samples

Table 4 summarizes the concentrations of the 16 EPA-regulated PAHs measured in the TURF B pilot leachate samples. Total measured PAH concentrations varied between 0.3 and 0.7 μg/L. The results are consistent with the results of published reports, summarized in Table 5.

Higher molecular weight PAHs (those with five and six benzene rings) were generally not present in artificial turf leachate, possibly because these compounds adhere too strongly to the rubber matrix to leach out. Overall, these results suggest that the potential for artificial turf to leach PAHs is small (total concentrations below 1 μg/L), with acenaphtalene, phenanthrene, and anthracene contributing most to the total.

Table 4. Concentrations (µg/L) of the 16 PAH compounds regulated by EPA in leachate samples from the TURF B pilot setup.

Sampling date	12/18/07	1/4/08	1/7/08	2/4/08	2/20/08	2/25/08
Compound						
Naphthalene	N/D	N/D	N/D	N/D	N/D	N/D
Acenaphthylene	0.179	0.122	0.138	0.211	0.026	0.110
Acenaphthene	N/D	N/D	N/D	N/D	N/D	N/D
Fluorene	N/D	N/D	N/D	N/D	N/D	N/D
Phenanthrene	0.027	0.223	0.095	N/D	0.154	0.117
Anthracene	0.038	0.276	0.159	0.167	0.170	0.187
Fluoranthene	N/D	N/D	N/D	N/D	N/D	N/D
Pyrene	0.027	N/D	N/D	N/D	N/D	N/D
Benzo[a]anthracene	0.018	0.054	N/D	0.20	N/D	N/D
Chrysene	N/D	N/D	N/D	N/D	N/D	N/D
Benzo[b]fluoranthene	N/D	N/D	N/D	N/D	N/D	N/D
Benzo[k]fluoranthene	N/D	N/D	N/D	N/D	N/D	N/D
Benzo[a]pyrene	N/D	0.012	N/D	0.144	N/D	0.085
Indeno[1,2,3-cd]pyrene	N/D	N/D	N/D	N/D	N/D	N/D
Dibenz[a,h]anthracene	N/D	N/D	N/D	N/D	N/D	N/D
Benzo[g,h,i]perylene	N/D	N/D	N/D	N/D	N/D	N/D
Sum	0.29	0.69	0.39	0.73	0.35	0.50

N/D – below the detection of limit of <0.002 µg/L.

Table 5. Concentrations (µg/L) of PAHs from leaching tests according to EN 12457 with L/S 10 on tire granulates (Westerberg and Macsik, 2001) and on tire shreds (Haoya, 2002).

Sample	Tire granulate	Tire shred	Tire granulate
Leaching pH	7	6.9	13.6
Compound			
Naphthalene	11	0.02	<0.29
Acenaphtylene	<0.14	<0.02	0.46
Acenaphten	<0.5	0.02	<0.5
Fluorene	<0.2	0.02	2.8
Phenanthrene	0.1	<0.02	<0.05
Anthracene	<0.01	<0.02	<0.01
Fluoranthene	<0.01	<0.02	0.09
Pyrene	<0.05	0.02	<0.06
Benzo(a)anthracene	0,03	<0.02	<0.01
Chrysene	<0.01	<0.02	<0.01
Benzo(b)fluoranthene	<0.01	<0.02	<0.04
Benzo(k)fluoranthene	<0.01	<0.02	<0.01
Benzo(a)pyrene	<0.01	<0.02	<0.02
Dibenz(a,h)anthracene	<0.01	<0.02	<0.01
Benzo(ghi)perylene	<0.05	<0.02	<0.06
Indeno(1,2,3-cd)pyrene	<0.01	<0.02	<0.01
Total-PAH	11	0.3	3.4

4.4. Field Site

4.4.1. Background sampling during the 2007-08 rainy season

To assess the impact of artificial turf on groundwater and surface water runoff, rainwater and soil water samples were collected and analyzed for metal content and total organic carbon (TOC). The sampling dates are summarized in Table 6.

Table 6. Sampling dates of the background samples in the 2007-08 rainy season.

Sampling Date	Rainwater (Stanford)	Rainwater (Field site)	Soil water (Stanford)
11/11/07	X		
12/04/07	X		
12/06/07	X		
12/17/07	X		X
12/18/07	X		X
12/20/07	X		X
12/28/07	X		
01/02/08	X		
01/04/08	X		
01/07/08	X		
01/09/08	X		
01/16/08	X		
02/04/08	X	X	
02/20/08	X	X	
02/21/08	X		
02/23/08	X	X	
02/25/08	X	X	
03/15/08	X		

Samples were taken during the 2007-2008 rainy season on a lawn and near the pilot setups located at Stanford University, and near the field sampling devices installed at the field site. The concentrations of major heavy metals and TOC contents in the rainwater, soil water, and artificial turf field leachate samples were measured, using the procedures given in the method section.

4.4.2. Heavy metals in rainwater and soil water

Rain and soil water samples were analyzed for a total of 24 elements: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, and V. Figure 26 shows the results of the heavy metal analyses in the soil water samples. In the rainwater, the concentrations of the heavy metals (Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, and V) were always below 0.005 mg/L, the method detection limit. Such low concentrations can be expected in regions without air pollution from heavy industry or power generation, such as San Jose.

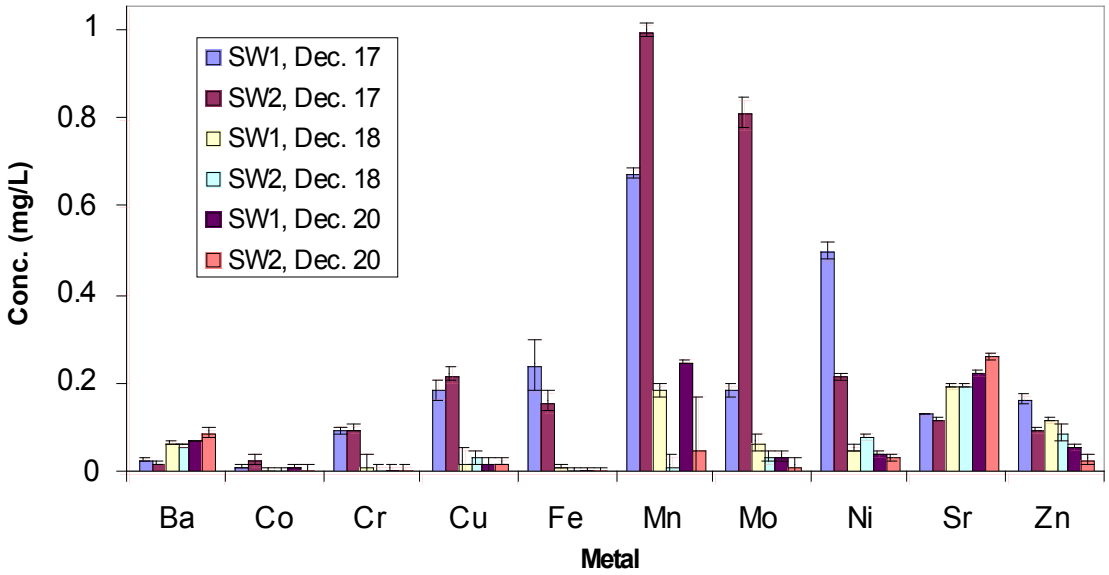

Figure 26. Concentrations of major heavy metal species found in the soil water samples.

Of the heavy metals analyzed, Mn, Mo, and Ni were found at the highest levels. Mn, which is an element frequently found in soils, was likely released from soil minerals. The sources of Mo and Ni are unknown.

4.4.3. TOC in rainwater and soil water

Figure 27 shows TOC levels in rainwater samples collected November 07 through February 08. The TOC levels in the field rainwater ranged from approximately 6 to 12 mg/L. At Stanford, rainwater TOC was generally lower (approximately 3 to 7 mg/L). The observed values exceed values reported for rainwater collected in San Diego (0.1 to 0.5 mg/L, Williams et al., 1991), perhaps because San Diego is located on the coast. The relatively high TOC levels in the field rainwater may be an anomaly that resulted from dry-deposition of organic materials (e.g., dust, organic compounds or pollens) in the sampling device.

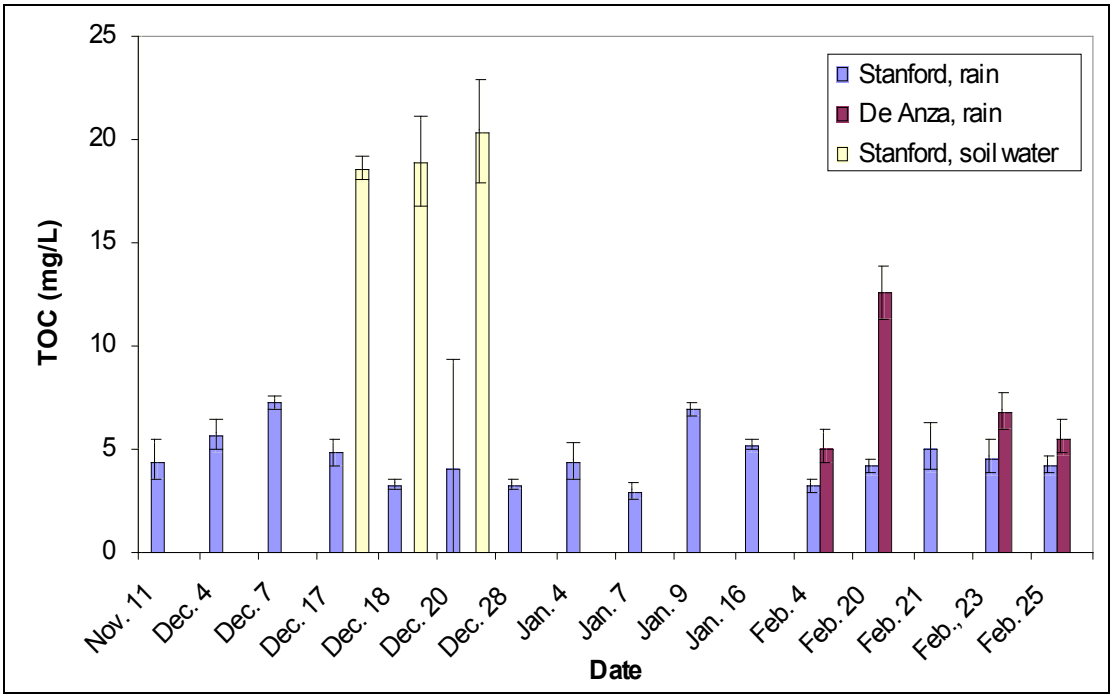

Figure 27. TOC levels in rainwater and soil water samples collected.

The TOC levels in the soil water samples are close to 20 mg/L, much higher than those in the rainwater, clearly indicating contribution of organic matter by soil. TOC in soil water likely originates from soil organic matter, such as decaying grass, roots, or leaves.

4.4.4. Heavy metals, TOC, and PAHs in the leachate from artificial turf

Figure 28a indicates the distribution of metal species detected in the leachate from artificial turf collected at the field site on February 20, 2008. Consistent with our observations from laboratory experiments and pilot setups discussed above, Zn was the major metal in leachate samples (approximately 100 times higher than all other heavy metals). Ba, Co, Cu, Fe, Mn, and Ni were present at concentrations near or above 0.005 mg/L, Co, Mn, and Ni, were close to the instrumental detection limits, and Ba, Cu, and Mn were detected but their presence was not statistically significant (at 99% CIs); an exception is Ba in the leachate from the right sampler.

Figure 28b shows the concentrations of Zn in the rainwater and in the leachate from the field site collected after four rain events that occurred consecutively. The concentration of Zn in the leachate ranged from 0.13 to 0.47 mg/L. Zn concentrations in the samplers on the left and right side of the field were different for unknown reasons. Perhaps the observed concentration differences were caused by different amounts of ground rubber present in the test plots (i.e., field scale heterogeneity). The concentrations of Zn in the leachate samples collected on February 20, 2008 were much higher than those collected on other days. An explanation for this discrepancy may be the long dry period (16 days) that preceded the rain event of February 20. During this time, degradation of rubber may have occurred because of exposure to sunlight and warming. The Zn concentration in samples Feb. 20, Feb. 23, and Feb 25 decreased with each rain event, consistent with decreasing Zn mobilization with shorter drying, warming, and irradiation intervals. Overall, these field data demonstrate that Zn is the dominant heavy metal released by crumb rubber contained in infill.

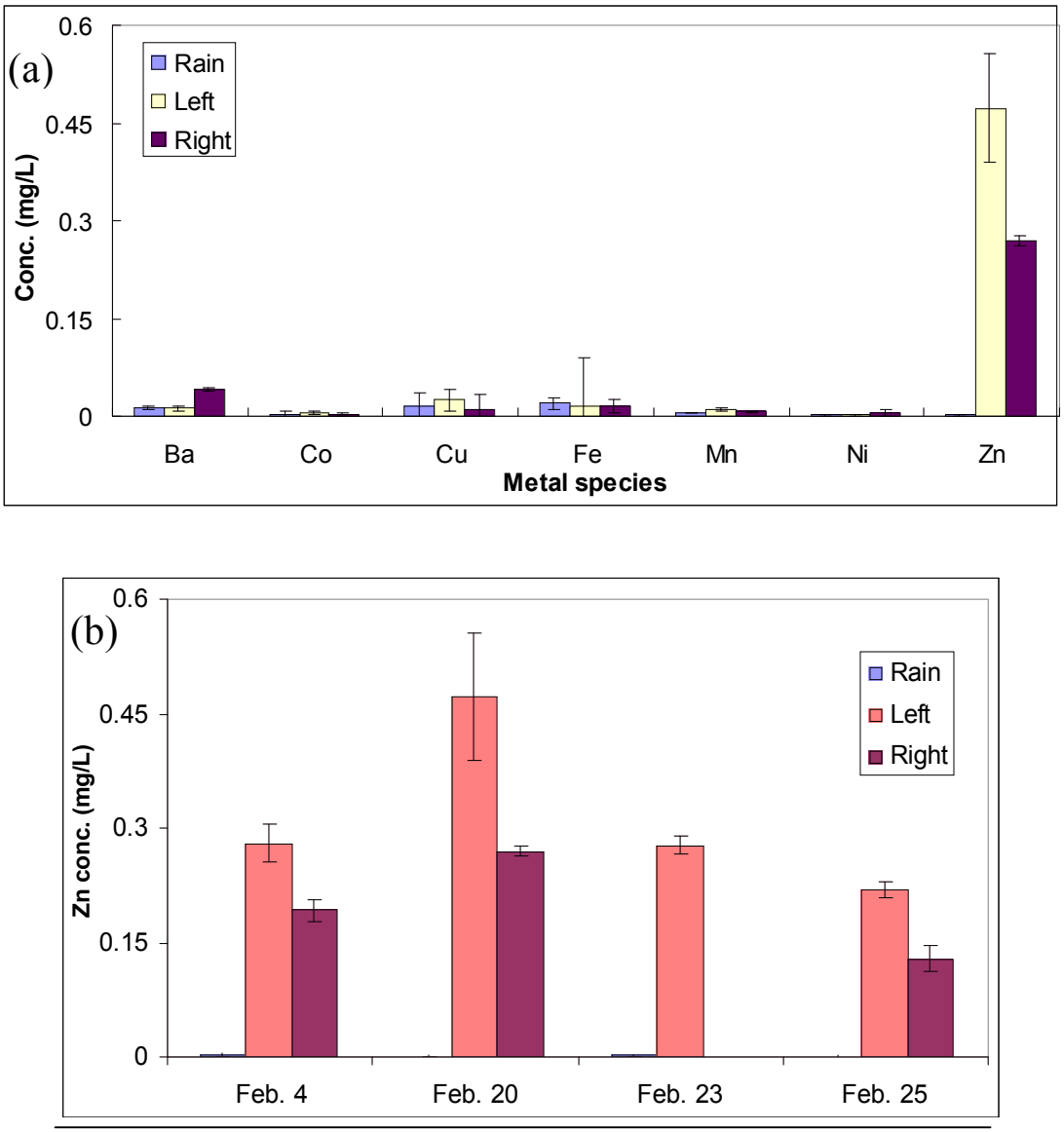

Figure 28. Zn concentrations in rain and leachate samples (sites L and R Figure 7) obtained from the field site: (a) concentrations of major metal species found in the leachate samples collected on 2/20/08; and (b) Zn concentrations in the leachate of four sequential raining events (no data for R on Feb. 23).

Figure 29 compares the TOC levels in the rainwater and in the leachate collected at the sampling points L and R of the field site. The TOC contents in the rainwater and the leachate ranged, on average, from 6 to 17 mg/L. In general, TOC levels in the leachate samples were 3 to 8 mg/L higher than those in the rainwater. As was observed

for Zn, TOC levels in the leachate samples collected from the right sample (Sample-R) were always higher than those from the left (Site-L). The TOC level in the leachate collected on February 20, 2008 were nearly twice as high as those collected before or after. We suspect that the higher TOC concentrations resulted from degradation of rubber as a result of weathering (i.e., exposure to sunlight and heat) or from the dry deposition of organic dust. The first flush of rainwater may have removed the readily leachable fraction of these materials. It is noteworthy that the rainwater TOC on Feb. 20 was much higher than on the three other sampling dates. This may have been caused by dust that was deposited in the samplers during the preceding dry-period, which was 16 days long. The Ecotoxicological significance of the data is difficult to assess without further research.

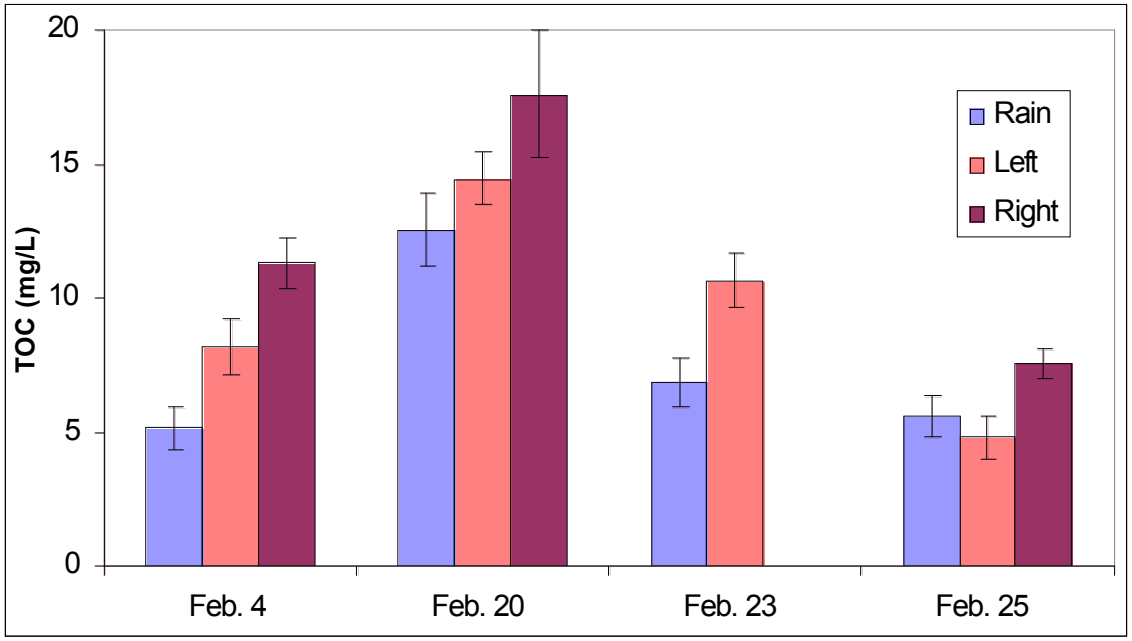

Figure 29. TOC concentrations in field samples.

Table 7 shows the concentrations of the 16 EPA-regulated PAHs in rainwater and leachate samples collected from the field site. Total PAH concentration in the samples varied from 0.12 to approximately 1.0 μg/L. These concentrations are within the ranges found in urban rainwater. Concentrations of PAHs in rainwater samples of Singapore, a coastal city with a high traffic volume, are shown in Table 8 for comparison. The PAHs

in the rainwater probably originate from incomplete combustion of fossil fuels by motor vehicles.

Table 7. Concentrations (µg/L) of the 16 PAH compounds regulated by EPA in rainwater and leachate samples collected from the field site.

Location	Rainwater	Site-L	Site-R	Site-L	Site-L	Site-R
Sampling date	2/4/08	2/4/08	2/4/08	2/20/08	2/25/08	2/25/08
Naphthalene	N/D	N/D	N/D	N/D	N/D	N/D
Acenaphthylene	N/D	N/D	N/D	0.314	N/D	N/D
Acenaphthene	0.009	0.023	0.030	0.009	0.010	0.019
Fluorene	N/D	N/D	N/D	N/D	N/D	N/D
Phenanthrene	0.292	0.045	0.017	0.071	0.218	0.223
Anthracene	0.390	0.057	0.028	0.074	0.205	0.211
Fluoranthene	0.180	0.031	0.029	0.048	0.134	0.116
Pyrene	0.020	N/D	N/D	N/D	0.006	0.006
Benzo[a]anthracene	N/D	N/D	N/D	0.212	0.003	N/D
Chrysene	0.034	0.006	0.006	N/D	N/D	N/D
Benzo[b]fluoranthene	0.015	0.009	0.009	N/D	0.040	0.017
Benzo[k]fluoranthene	0.014	N/D	N/D	N/D	N/D	N/D
Benzo[a]pyrene	N/D	N/D	N/D	N/D	N/D	N/D
Indeno[1,2,3-cd]pyrene	N/D	N/D	N/D	N/D	N/D	N/D
Dibenz[a,h]anthracene	N/D	N/D	N/D	N/D	N/D	N/D
Benzo[g,h,i]perylene	N/D	N/D	N/D	N/D	N/D	N/D
Sum	0.95	0.17	0.12	0.73	0.62	0.59

N/D – below the detection of limit of <0.002 µg/L.

Table 8. Concentrations (µg/L) of PAHs detected in rainwater samples in Singapore reported by Basheer et al. (2003)

Location	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
Naphthalene	0.022	0.061	0.162	0.008	0.067	0.041
Acenaphthylene	0.044	0.005	0.007	0.014	0.005	0.005
Acenaphthene	0.022	0.008	0.029	0.004	0.007	0.024
Fluorene	0.08	0.057	0.054	0.068	0.064	0.059
Phenanthrene	0.021	0.013	0.012	0.006	0.013	0.006
Anthracene	0.041	0.009	0.013	0.012	0.012	0.011
Fluoranthene	0.027	0.005	0.005	0.01	0.014	0.026
Pyrene	0.049	0.008	0.008	0.017	0.006	0.005
Benz[a]anthracene	0.029	0.013	0.023	0.038	0.037	0.044
Chrysene	0.033	0.009	0.009	0.014	0.013	0.007
Benzo[a]fluoranthene	0.05	0.026	0.012	0.036	0.006	0.025
Benzo[k]fluoranthene	0.033	0.022	0.055	0.039	0.028	0.043
Benzo[a]pyrene	0.066	0.021	0.08	0.051	0.04	0.165
Indenol[1,2,3-cd]-pyrene	0.071	0.063	0.051	0.088	0.042	0.052
Dibenz[a,h]anthracene	0.036	0.039	0.055	0.036	0.044	0.039
Benzo[ghi]perylene	0.049	0.055	0.041	0.048	0.042	0.052
Total PAH	0.67	0.41	0.62	0.49	0.44	0.60

4.5. Geochemical Modeling

Preliminary Geochemical modeling shows that the anions (at the concentration ranges expected in rainwater and artificial turf leachate) should have negligible impact on Zn speciation in the leachate (Appendix A). This is evidenced by speciation curves not being sensitive to the concentrations of Cl^-, SO_4^{2-}, and total carbonate species$^-$ that are 100 times higher than those commonly occurring in rainwater. On the other hand, modeling shows, that the interactions of Zn with the solid phase materials can be expected to play a key role in determining its aqueous concentration. This is consistent with the observed attenuation during passage of leachate through the rock material layers below the artificial turf.

Geochemical modeling was used to evaluate possible phases that may be controlling the Zn concentration of leachate in contact with carbonaceous rock materials. Figure 30 shows the Zn concentrations in the leachate discharged from the pilot setups and the total concentration of aqueous Zn species controlled by the solubility of hydrozincite and smithsonite in the presence of calcite predicted by speciation modeling. After passing through the rock materials, Zn concentrations in the leachate decreased to below 10^{-7} mol/L (0.007 mg/L). One possible mechanism causing the significant drop in Zn^{2+} concentration is precipitation/co-precipitation at the surface of carbonate rock minerals, particularly calcite (Sibrell et al., 2007; Zachara, et al., 1989). However, the aqueous Zn^{2+} concentration limited by precipitation would be approximately 4×10^{-6} mol/L, which is more than one order of magnitude higher than the Zn^{2+} concentrations observed in the leachate discharged from pilot setups.

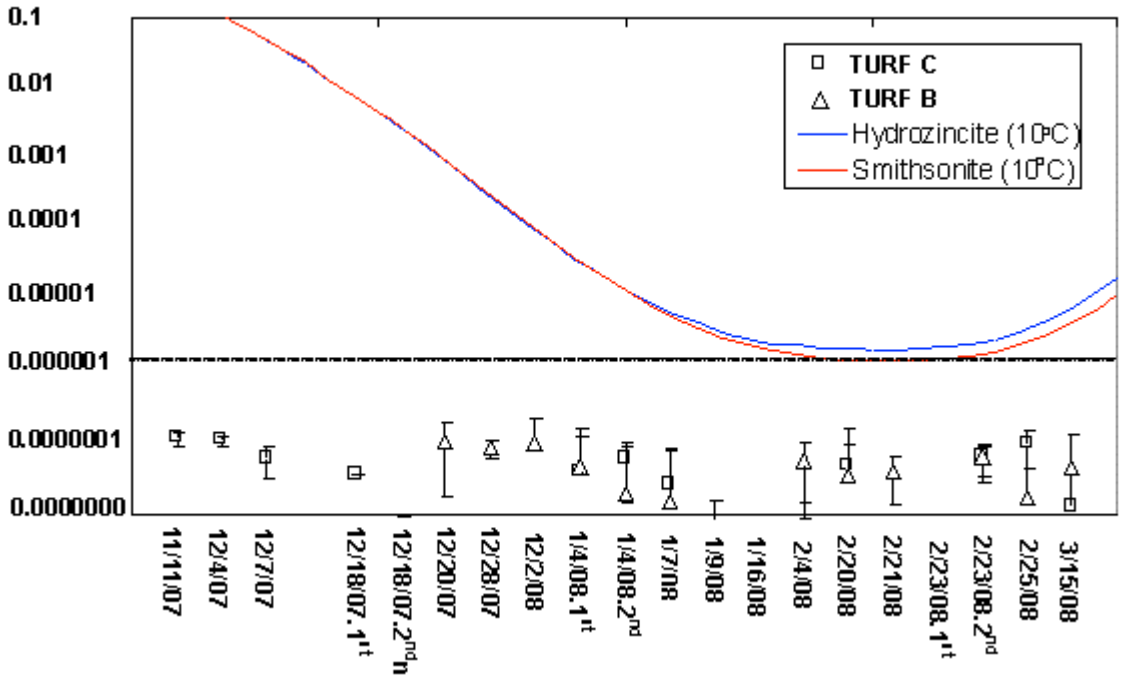

Figure 30. Comparison of Zn concentration in leachate discharged from the TURF C and TURF B pilot setups with the total concentration of aqueous Zn^{2+} species controlled by precipitation as smithsonite ($ZnCO_3$) and hydrozincite ($Zn_5(OH)_6(CO_3)_2$). The line indicates the solubility limit of smithsonite.

The fact that the Zn^{2+} concentrations in the leachate after passing through the rock materials were lower than the expected value based on solubility control ($ZnCO_3$ and $Zn_5(OH)_6(CO_3)_2$) suggests that sorption may have played an important role in the leachate-rock interactions. Competition has been observed among multiple solid phases for zinc sorption. Amorphous iron oxyhydroxide and goethite out-compete carbonate and silicate phases for zinc, while in iron-free systems, zinc is associated with carbonate and silicate phases (Carroll et al., 1998; Zachara et al., 1988 & 1989; Elzinga and Reeder, 2002). In particular, the ionic radius of Zn^{2+} is 25% smaller than that of Ca^{2+} (Reeder et al., 1987), it can substitute for Ca^{2+} in the surface layer of calcite (Cheng et al., 1998; Temmam et al., 2000), and adsorb on its surface via formation of mononuclear inner-

sphere adsorption complexes (Elzinga and Reeder, 2002). Given the significant amount of rock materials (7-9-inch thick layer) present below the artificial turf, the near 100% retention of Zn released from the ground rubber in one rainy season is not surprising.

4.6. Environmental Significance of Metal Contents in Artificial Turf Components

The heavy metal content was determined in the components of artificial turf, i.e., the crumb rubber infill, fiber blade material, and carpet backing. Zn contents in fresh crumb rubber supplied by two major manufacturers were approximately 20 mg/g. The other metals tested were present in substantially lower levels. Several fiber blade materials and carpet backing were also tested and indicated relatively low metal concentrations, suggesting that these materials are not likely sources of heavy metal contamination. In rubber crumb leachate, Zn was by far the most abundant metal. Leaching rates of Zn increased with decreasing pH, and with duration of exposure to heat and sunlight. The quantities leached in synthetic acid rainwater (pH 3.4-3.5) were significantly (up to 50%) higher than in rainwater or purified laboratory (Milli-Q) water at a circumneutral pH.

Table 9 compares the contents of Cu, Ni, Pb, and Zn measured in the crumb rubber with the geometric means of the contents of these metals contents in U.S. surface soils (mineral soils) in selected states.

Table 9. Arithmetic mean value and range of Cu, Ni, Pb, and Zn measured in three samples of crumb rubber samples from different sources.

Heavy metal	Cu (mg/kg) #	Ni (mg/kg) #	Pb (mg/kg) #	Zn (mg/kg) *
TURF A-1	8.3	2.7	44	21,300 *
	7.6-8.6	2.5-2.9	33-56	20,300-22,500 *
TURF A-2	8.2	2.4	27	18,800 *
	7.6-9.2	2.3-2.4	9.3-36	17,100-23,300 *
TURF B-1	37	2.7	68	21,400 *
	29-42	2.4-2.9	59-79	18,300-26,600 *
TURF B-2	24	2.4	15.0	20,600 *
	21-25	2.2-2.5	13-17	18,300-22,100 *
GI	52	2.6	30	13,800 &
	44-63	2.2-3.1	12-44	13,400-14,300
GR	17	3.1	18	14,000 &
	14-20	3.0-3.2	8.6-30	13,500-14,300
OG	21	2.7	8.6	18,700 &
	19-22	2.3-2.9	5.8-11	17,800-19,900
MH	30	2.8	4.3	20,800 &
	25-35	2.5-3.1	3.7-5.3	20,000-21,300

Number of determinations:

: triplicate samples, each measured once.

* : triplicate samples, each measured twice.

& : triplicate samples, each measured 6 times.

Holmgren et al. (1993) analyzed Cu, Ni, Pb, and Zn in California soil and found average values of 37.3, 50.5, 9.7, and 82.7 mg/kg, respectively. On average, Zn contents in crumb rubber are approximately 200 times higher than in soils. Because Zn can leach from crumb rubber, artificial turf fields that employ crumb rubber cushioning should be regarded as potential point sources for Zn. However, rock materials supporting artificial turf fields attenuate Zn discharge by storm runoff by strongly adsorbing dissolved Zn.

Whether the sorption capacity is sufficient to prevent Zn release into the environment for the duration of artificial turf fields remains to be investigated.

The Pb values in crumb rubber were variable and in most cases higher than the average content reported for California soils (9.7 mg/kg). Pb concentrations in samples from artificial turf fields (GI, GR, and OG) varied widely (by a factor of two to three within sites and by a factor of seven overall), suggesting that the Pb content in crumb rubber from different sources varies. Different leaching rates at different locations may also contribute to the observed differences in Pb content. For Cu and Ni, the observed contents are lower in crumb rubber that California soil on average.

U.S. EPA has established an MCL for dinking water for benzo(a)pyrene of 0.2 µg/L, while MCLs for other PAHs have not been established. U.S. EPA has established water quality criteria (Table 10) for the protection of human health from exposure to PAHs in drinking water and in the tissue of edible aquatic organisms (e.g., fish). Based on the concentrations of PAHs detected in the leachate samples, PAHs are generally not of significant concern.

Table 10. Water quality criteria for the protection of human health from exposure to PAHs in drinking water and in the tissue of edible aquatic organisms.

Contaminant	Consumption of water and organisms (e.g., fish)[#], μg/L	Consumption of organisms (e.g., fish) only[#], μg/L
Anthracene	9,600	110,000
Fluorene	1,300	14,000
Acenaphthene	1,200	2,700
Benzo(a)anthracene	0.0044*	0.049*
Fluoranthene	300	370
Pyrene	960	11,000
Chrysene	0.0044*	0.049*
Benzo(a)pyrene	0.0044*	0.049*

— from USEPA (2005);

* — based on a 1-in-1-million (10-6) cancer risk.

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6. GLOSSARY

Abs	absorbance
ASME	American Society of Mechanical Engineers
BAT	best available technology
EMPA	electron microprobe analysis
EPA	Environmental Protection Agency
FID	flame ionization detector
ICP-AES	inductively coupled plasma atomic emission spectroscopy
QA/QC	quality assurance/quality control
SEM	scanning electron micrography

APPENDIX A

Modeling Speciation of Zn in Artificial Turf Leachate

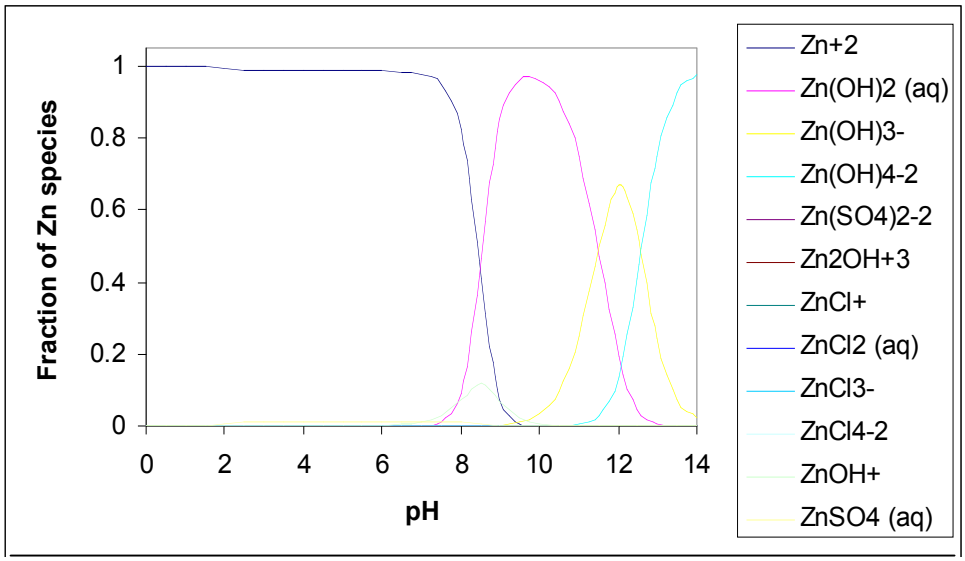

Figure A1. Zn speciation in a hypothetical system in the absence of carbonate species, where $[Zn^{2+}]_T$ = 1.6 mg/L. Other ionic species compositions: $[Cl^-]$ = 17 mg/L, $[SO_4^{2-}]$ = 7.6 mg/L, $[Ca^{2+}]$ = 0.8 mg/L, $[Mg^{2+}]$ = 1.2 mg/L, $[Na^+]$ = 9.4 mg/L.

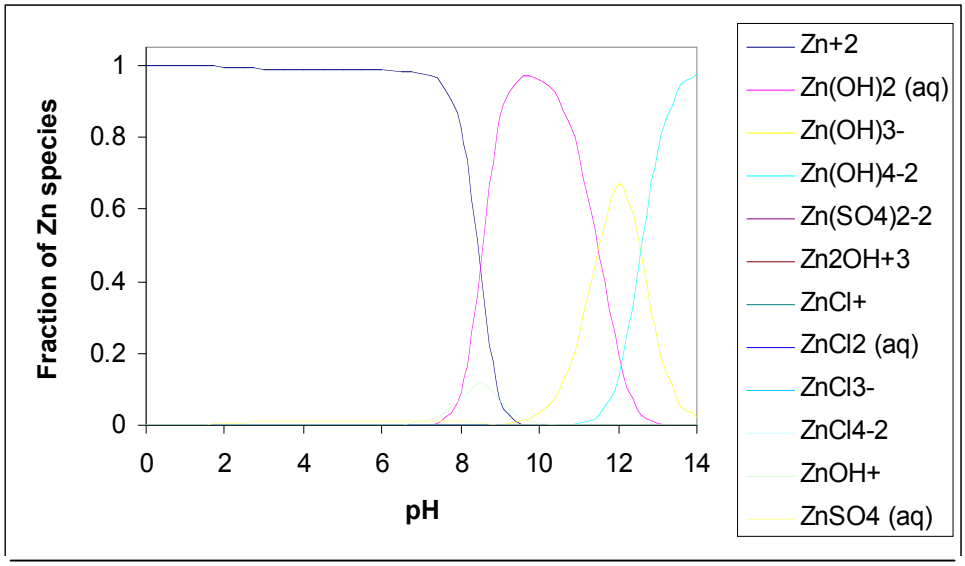

Figure A2. Zn speciation in a hypothetical system in the absence of carbonate species, where $[Zn^{2+}]_T$ = 16 mg/L. Other ionic species compositions: $[Cl^-]$ = 17 mg/L, $[SO_4^{2-}]$ = 7.6 mg/L, $[Ca^{2+}]$ = 0.8 mg/L, $[Mg^{2+}]$ = 1.2 mg/L, $[Na^+]$ = 9.4 mg/L.

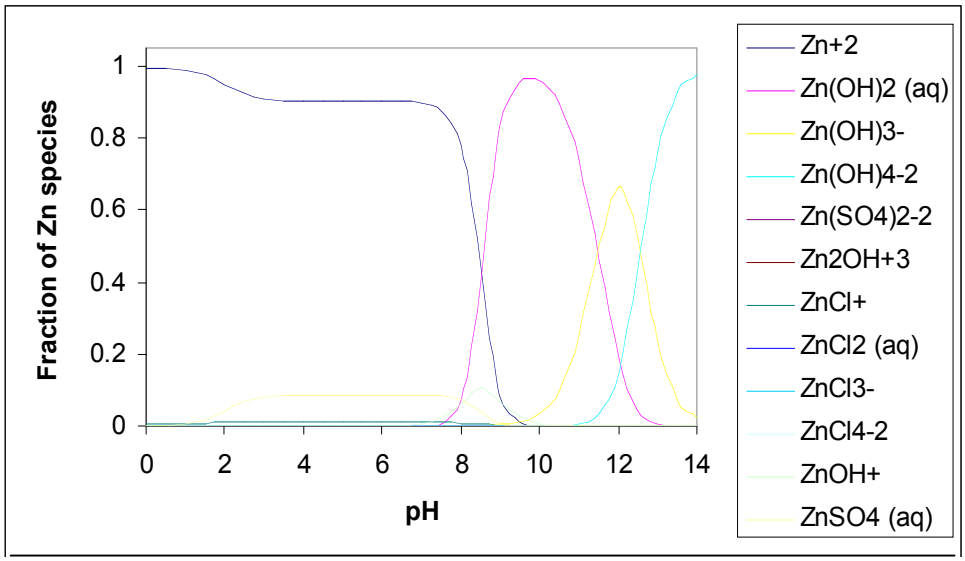

Figure A3. Zn speciation in a hypothetical system in the absence of carbonate species, where $[Zn^{2+}]_T$ = 1.6 mg/L. Other ionic species compositions: $[Cl^-]$ = 170 mg/L, $[SO_4^{2-}]$ = 76 mg/L, $[Ca^{2+}]$ = 0.8 mg/L, $[Mg^{2+}]$ = 1.2 mg/L, $[Na^+]$ = 9.4 mg/L.

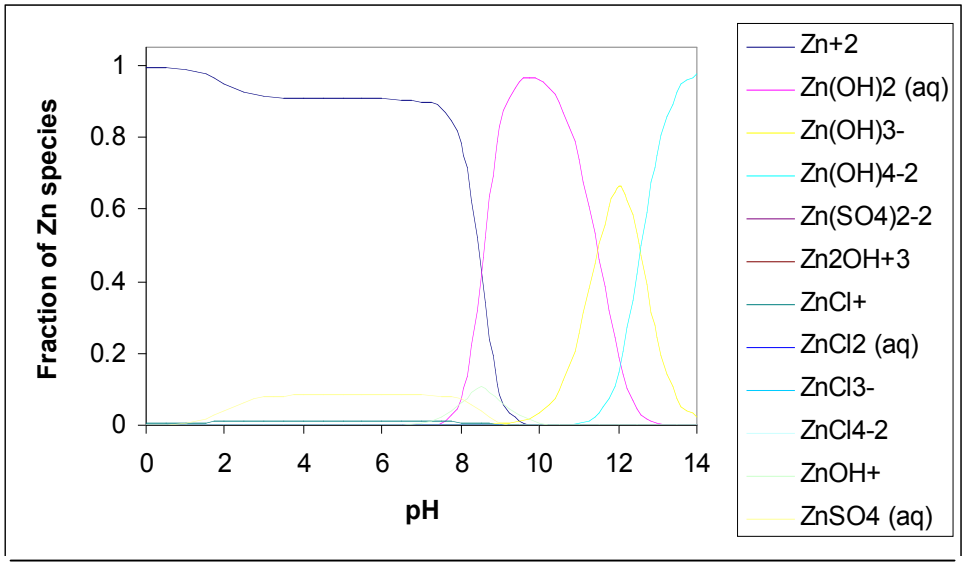

Figure A4. Zn speciation in a hypothetical system in the absence of carbonate species, where $[Zn^{2+}]_T$ = 16 mg/L. Other ionic species compositions: $[Cl^-]$ = 170 mg/L, $[SO_4^{2-}]$ = 76 mg/L, $[Ca^{2+}]$ = 0.8 mg/L, $[Mg^{2+}]$ = 1.2 mg/L, $[Na^+]$ = 9.4 mg/L.

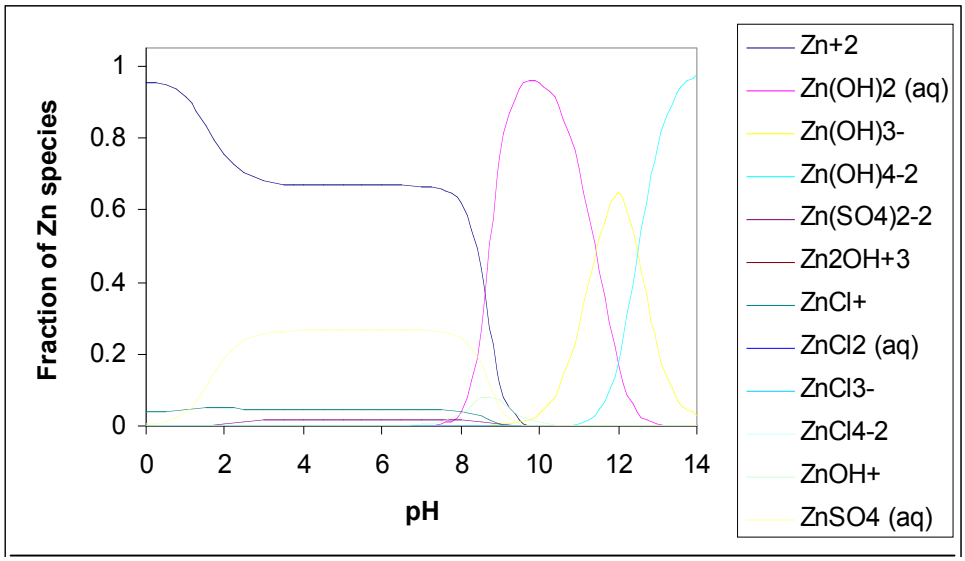

Figure A5. Zn speciation in a hypothetical system in the absence of carbonate species, where $[Zn^{2+}]_T$ = 1.6 mg/L. Other ionic species compositions: $[Cl^-]$ = 1700 mg/L, $[SO_4^{2-}]$ = 760 mg/L, $[Ca^{2+}]$ = 0.8 mg/L, $[Mg^{2+}]$ = 1.2 mg/L, $[Na^+]$ = 9.4 mg/L.

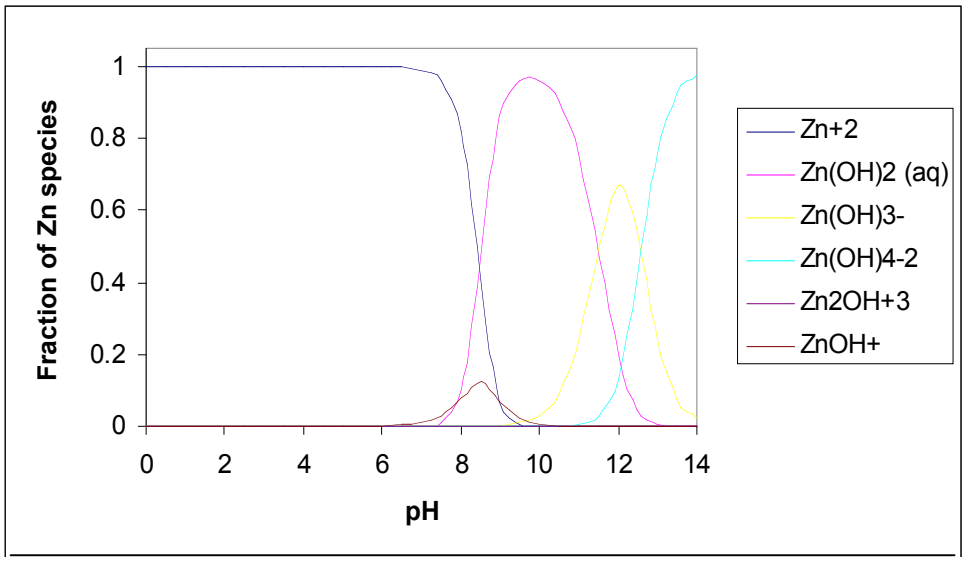

Figure A6. Zn speciation in pure water, where $[Zn^{2+}]_T$ = 1.6 mg/L.

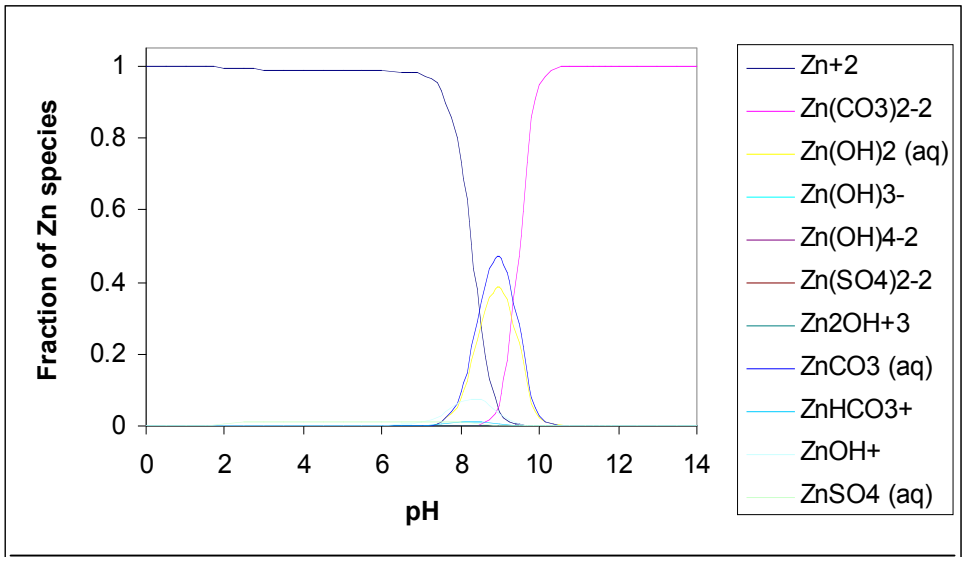

Figure A7. Zn speciation in typical rainwater water in a closed system, where $[Zn^{2+}]_T$ = 1.6 mg/L. Other ionic species compositions: $[Cl^-]$ = 17 mg/L, $[SO_4^{2-}]$ = 7.6 mg/L, $[Ca^{2+}]$ = 0.8 mg/L, $[Mg^{2+}]$ = 1.2 mg/L, $[Na^+]$ = 9.4 mg/L, $[CO_3^{2-}]$ = 4.0 mg/L.

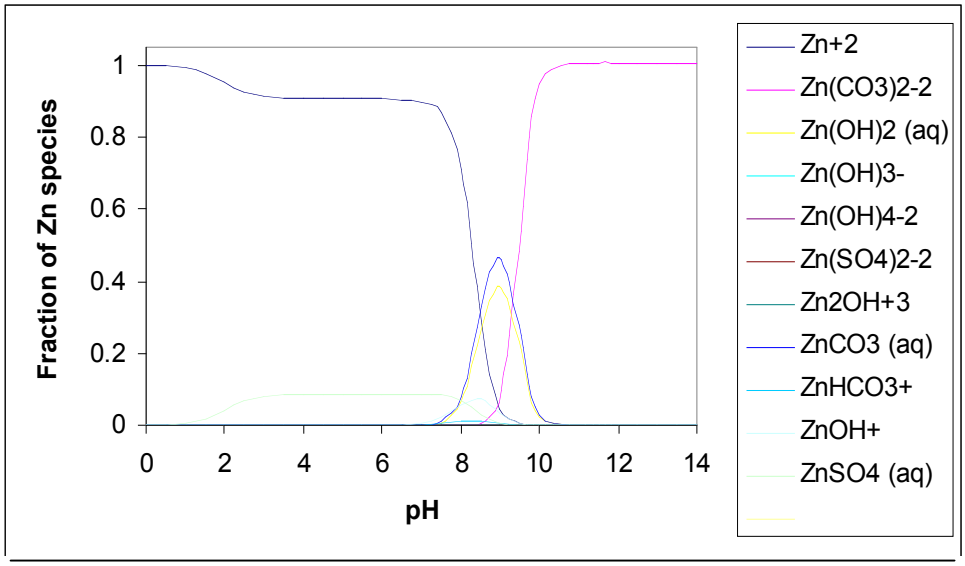

Figure A8. Zn speciation in typical rainwater water in a closed system, where $[Zn^{2+}]_T$ = 1.6 mg/L. Other ionic species compositions: $[Cl^-]$ = 170 mg/L, $[SO_4^{2-}]$ = 76 mg/L, $[Ca^{2+}]$ = 0.8 mg/L, $[Mg^{2+}]$ = 1.2 mg/L, $[Na^+]$ = 9.4 mg/L, $[CO_3^{2-}]$ = 40 mg/L.

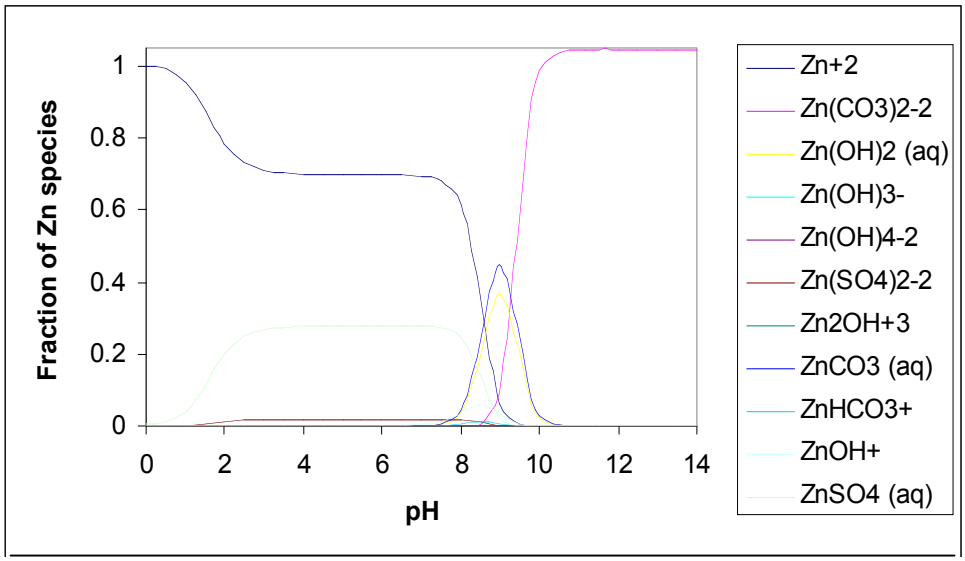

Figure A9. Zn speciation in typical rainwater water in a closed system, where $[Zn^{2+}]_T$ = 1.6 mg/L. Other ionic species compositions: $[Cl^-]$ = 1700 mg/L, $[SO_4^{2-}]$ = 760 mg/L, $[Ca^{2+}]$ = 0.8 mg/L, $[Mg^{2+}]$ = 1.2 mg/L, $[Na^+]$ = 9.4 mg/L, $[CO_3^{2-}]$ = 400 mg/L.

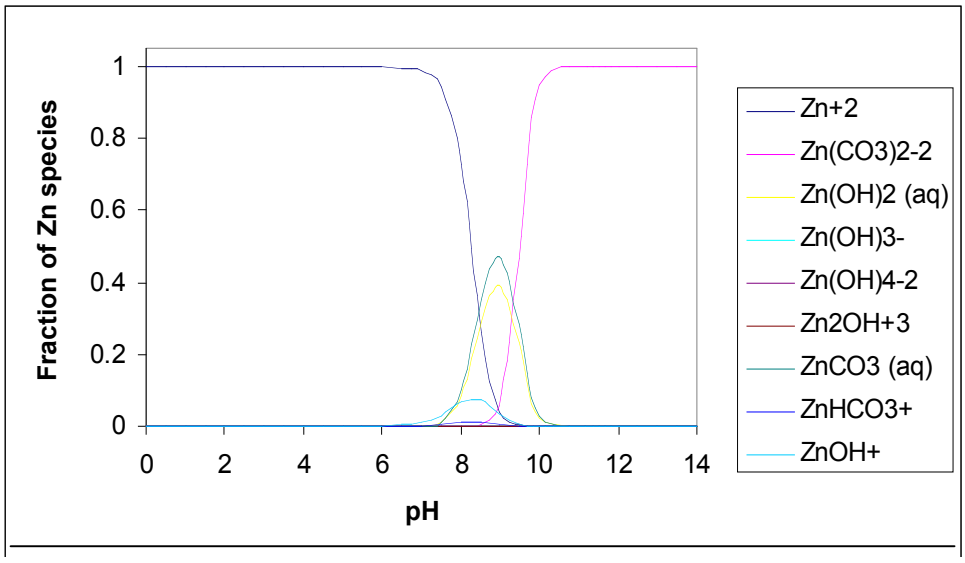

Figure A10. Zn speciation in pure water in an open system (i.e., in equilibrium with atmospheric CO_2), where $[Zn^{2+}]_T$ = 1.6 mg/L.

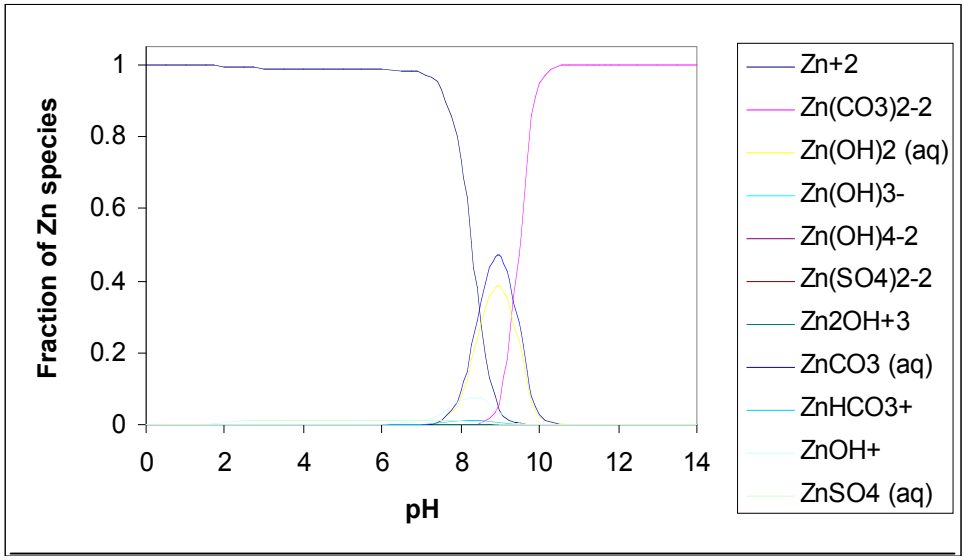

Figure A11. Zn speciation in typical rainwater water in an open system (i.e., in equilibrium with atmospheric CO_2), where $[Zn^{2+}]_T$ = 1.6 mg/L. Other ionic species compositions: $[Cl^-]$ = 17 mg/L, $[SO_4^{2-}]$ = 7.6 mg/L, $[Ca^{2+}]$ = 0.8 mg/L, $[Mg^{2+}]$ = 1.2 mg/L, $[Na^+]$ = 9.4 mg/L, $[CO_3^{2-}]$ = 4.0 mg/L.

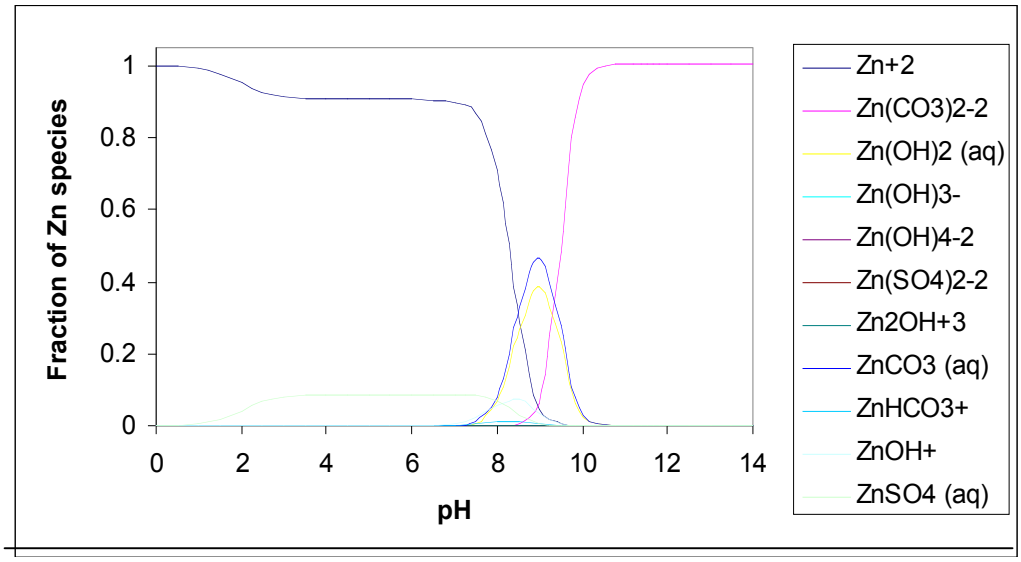

Figure A12. Zn speciation in typical rainwater water in an open system (i.e., in equilibrium with atmospheric CO_2), where $[Zn^{2+}]_T$ = 1.6 mg/L. Other ionic species compositions: $[Cl^-]$ = 170 mg/L, $[SO_4^{2-}]$ = 76 mg/L, $[Ca^{2+}]$ = 0.8 mg/L, $[Mg^{2+}]$ = 1.2 mg/L, $[Na^+]$ = 9.4 mg/L, $[CO_3^{2-}]$ = 40 mg/L.

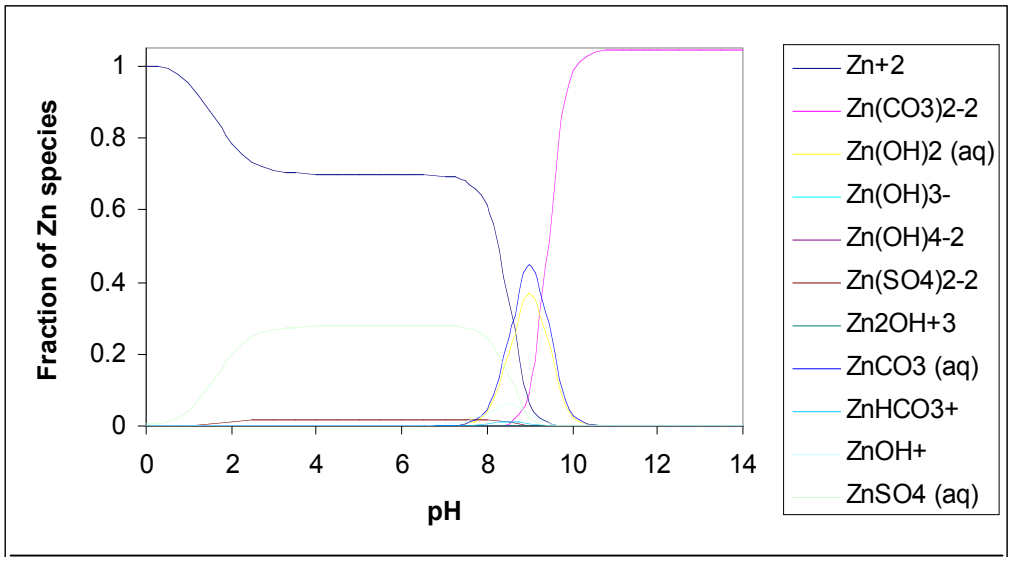

Figure A13. Zn speciation in typical rainwater water in a closed system, where $[Zn^{2+}]_T$ = 1.6 mg/L. Other ionic species compositions: $[Cl^-]$ = 1700 mg/L, $[SO_4^{2-}]$ = 760 mg/L, $[Ca^{2+}]$ = 0.8 mg/L, $[Mg^{2+}]$ = 1.2 mg/L, $[Na^+]$ = 9.4 mg/L, $[CO_3^{2-}]$ = 400 mg/L.

The following conclusions can be drawn from the comparison of the above Zn speciation diagrams (Figures A1-A13):

1. All Zn species are dissolved in aqueous phase in the concentration range (<10 mg/L) expected in leachate from artificial turf;
2. The total Zn concentration does not affect the speciation behavior in the concentration range (<10 mg/L) expected in leachate from artificial turf;
3. In the absence of carbonate species, Zn speciation is controlled by complexes with OH- at pH>8 in all water matrix;
4. In the presence of carbonate species, Zn speciation is controlled by complexes with CO_3^{2-} at pH>10;
5. Zn does not form any significant complexes with Cl- under all conditions studied, and Cl- is not expected to affect Zn speciation;
6. At pH<7, Zn speciation is only affected by SO42-, but no other anions;

7. Between pH 1 and 9, complexes of Zn2+ with SO42- can be important. However, at 7.6 mg/L SO42- (typical concentration in rainwater), only <1.3% of the total Zn resides as ZnSO4(aq); at 76 mg/L SO42-, <10% of total Zn resides as ZnSO4(aq), and even at 760 mg/L SO42-, >66% of Zn is still present in Zn2+ form in aqueous phase;
8. Anions have negligible impact on Zn speciation if present within the typical concentration ranges of rainwater and artificial turf leachate.